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## CONTRACT RESEARCH PROJECT REPORT

Quartermaster Food and Container Institute for the Armed Forces, Chicago  
QM Research and Engineering Command, QM Research and Engineering Center,  
Natick, Mass.

Nuclear Science and Engineering Corp.  
Pittsburgh, Pennsylvania

Project No.: 7-84-01-002  
Contract: DA-19-129-QM-1601

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(OF 5120)  
File No.: S-603  
Report No.: 3 (Final)  
Period: 10 May 60 - 9 Feb 61  
Initiation Date: 10 May 60

TITLE OF CONTRACT: Activation Analysis of Foods for Characterization  
of the Induced Radioactivities

### SUMMARY:

A program has been initiated to determine by neutron activation analysis the elemental concentrations of a wide variety of elements in four (4) foods: beef, pork, ham, and chicken. The resulting analytical data, combined with concurrent determinations of radioactivity balances for each food, will provide a basis for radiochemical characterization of the neutron-induced activities found or expected to be found in foods after sterilization at the several types of irradiation facilities.

Ash residues from homogenized samples of the four foods have been analyzed in two irradiation experiments. Data are reported for qualitative analyses of eight (8) elements in each food and quantitative analytical data are reported for twenty (20) additional elements. Of the elements determined, phosphorus, with concentrations in the bulk foods of  $\sim 0.1$  per cent, was the most abundant. Values of other trace element concentrations were as small as  $10^{-5}$  ppm.

Radioactivity balance studies are being performed on the four ash samples from the second irradiation. In the period from 13 days to 125 days after irradiation, the major constituents of the total beta radioactivity in these samples were 14.2-day  $P^{32}$  and 87-day  $S^{35}$ . The major contribution to the observed total gamma radioactivity are bremsstrahlung from  $P^{32}$  along with 45-day  $Fe^{59}$ , 245-day  $Zn^{65}$  and 5.2-year  $Co^{60}$ .

## INTRODUCTION

NSEC is carrying out a program, under Project No. 7-84-01-002, to perform activation analysis of foods for elements which yield radioactive species when subjected to neutron irradiation. Emphasis is being placed on the determination of the concentrations of elements having expected concentrations of 1 ppm or more in four foods: beef, ham, pork, and chicken. The respective foods to be studied have been prepared by the Quartermaster Food and Container Institute so that they are representative of those portions normally issued for human consumption by the armed forces, with the exception that the foods were homogenized to facilitate acquisition of statistically significant samples for analysis.

The data resulting from this program are to be compared with analytical data already available for foods<sup>(1)</sup> and with food irradiation data obtained in a previous program<sup>(2)</sup>. This comparison will assist in the radiochemical characterization of the neutron-induced radioactivities found or expected to be found in these foods after sterilization in the several types of food-irradiation facilities.

Activation analysis may be defined<sup>(3)</sup> as a method of determining the concentration of an element in a matrix by measuring the characteristic radiations emitted by a radioactive nuclide resulting from a specific nuclear reaction in the trace element. This radioactive reaction product, or activation product, possesses a unique combination of physical, chemical, and nuclear properties. These properties provide the necessary specificity for its identification and measurement.

Neutron activation analysis was selected as the method of analysis for trace elements in the foods of interest in this program for two principal reasons:

(1) the method provides the high degree of specificity and sensitivity required for measurement of the very low elemental concentrations expected, and (2) characterization of the neutron activation products utilized in this program will provide data for estimating the concentrations of neutron-induced radioactivities which may result from sterilization of these foods at the several types of food-irradiation facilities.

The detailed information for the individual constituents comprising the total radioactivity content induced in these foods by the known neutron fluxes will provide a basis for computing the radioactivities which can be induced during sterilization using the experimentally determined neutron fluxes<sup>(1)</sup> for the various irradiation-sterilization facilities.

### THEORETICAL CONSIDERATIONS

The general method of neutron activation analysis involves the irradiation of the samples to be assayed in an appropriate neutron flux to produce the desired activation products in sufficient quantity for accurate measurement, followed by post-irradiation radiometric analyses for the activation products. Generally, standard samples, or comparators, containing known quantities of the trace elements to be determined, are irradiated and analyzed concurrently with the matrix samples.

The production<sup>(1)</sup> of an activation product in both the matrix and the comparator samples proceeds according to equation (1)

$$D(t) = \phi n \sigma (1 - e^{-\lambda t}) \quad (1)$$

where  $D(t)$  = the quantity of the radioactive species in the sample at the end of irradiation, disintegrations per second

$\phi$  = the neutron flux,  $n/\text{cm}^2\text{-sec}$

$n$  = the number of atoms of the target nuclide in the irradiation sample

$\sigma$  = the activation cross-section,  $\text{cm}^2/\text{atom}$

$\lambda$  = the decay constant of the nuclide =  $\left[ \frac{0.693}{\text{half-life}} \right] \text{sec}^{-1}$

$t$  = the irradiation time, sec

The experimentally determined disintegration rates for the nuclide in the matrix and comparator samples along with the known quantities of the trace elements in the comparators provides the necessary data to determine the concentrations of the trace element in the matrix sample<sup>(4)</sup>, as shown in equation (2),

$$m_s = \frac{m_c D(t)_s}{D(t)_c} \quad (2)$$

where  $m_s$  and  $m_c$  are the masses of the trace element in the matrix sample and comparator, respectively, and  $D(t)_s$  and  $D(t)_c$  are the respective disintegration rates of the activation product.

The performance of a neutron activation analysis requires consideration of a set of six operations<sup>(3)</sup>: (1) the selection of an appropriate neutron-induced activation reaction; (2) the specification of materials for comparator samples; (3) the choice of a suitable irradiation facility; (4) the preparation of the samples for irradiation; (5) the irradiation and the post-irradiation analyses; and (6) the evaluation of the experimental data.

The feasibility of each of these operations was reviewed prior to selection of neutron activation analysis for the trace elements to be determined in this program. Some elements were selected, or excluded from the scope of work, on the basis of some of these considerations. A summary of the effects of these considerations on the determination of the scope of work is presented in the following sections.

### Selection of Activation Reactions

The first consideration in performing a neutron activation analysis for a trace element in a given matrix is the selection of the optimum activation reaction. Five factors must be taken into account in this selection<sup>(3)</sup>: (1) the suitability of the activation product, (2) the feasibility of performing the irradiation and the post

irradiation assays, (3) the analytical sensitivity achievable using the reaction, (4) the absence of competing activation reactions in the trace elements, and (5) the extent to which interfering reactions in the matrix may produce or consume the activation product to be assayed.

#### Suitability of activation products

The criteria for the nuclear properties of a suitable activation product, with special emphasis on the requirements for this program, have been delineated in a previous report<sup>(1)</sup>. In summary, the activation product (1) must be radioactive, (2) must have a half-life sufficiently long to permit the requisite post-irradiation radiometric analyses, but not so exceptionally long that it is produced only in such insignificantly small quantities that the achievable sensitivity or accuracy of the method is of no practical interest, and (3) there must be a naturally-occurring stable isotope in which the activation reaction can be induced. These considerations have led to the exclusion of certain elements<sup>(1)</sup> from the scope of work, since it has been shown that their analysis is not feasible by neutron activation.

In addition to the nuclear properties of the activation product, certain of its physical and chemical properties are important. For example, if the activation product is a gas or a highly volatile element, or if it may combine chemically with another constituent of the matrix to form a volatile compound, it may be released from the sample during the irradiation, thus compromising the analytical data. Therefore, activation reactions producing volatile radionuclides should be avoided whenever possible.

### Experimental feasibility

All of the considerations which diminish the suitability of the activation product have deleterious effects on the feasibility of performing the post-irradiation analyses. However, additional factors, such as excessive production of radiation-induced volatiles in the matrix, or the irradiation of volatile or explosive matrices in a nuclear reactor, may prevent the use of neutron activation analysis for such materials. These factors are not important for irradiation of food ash, but would impose considerable difficulties in the performance of neutron activation analysis of bulk foods. This consideration, along with the saving in irradiation costs due to volume reduction, was important in this program, in selecting the food ash as the matrix for irradiation.

### Analytical sensitivity

The analytical sensitivity achievable, using a specific neutron activation reaction, for a trace element in the four foods was estimated from an existing tabulation of standard sensitivities<sup>(3)</sup>. No selection of activation reactions for this program was significantly affected by sensitivity estimates, except for those cases wherein an extreme long half-life imposed practical limitations on the measurement of the activation product.

### Competing nuclear reactions

A competing nuclear reaction has been defined<sup>(3)</sup> as a reaction which yields a radionuclide isotopic with the activation product being used in the analysis. The experimental and instrumental techniques used in performing the post-irradiation analyses in this program are sufficient to preclude any serious effects due to competing reactions. Therefore, this consideration was not important in the specification of activation reactions.



### Interfering nuclear reactions

An interfering reaction has been defined<sup>(3)</sup> as a nuclear reaction in a constituent of the matrix, other than the trace element of interest, which produces or consumes the activation product to be assayed. An interfering reaction may change significantly the quantity of the activation product to be measured and, thus, produce an erroneous result. Two types of reactions may cause such interference:

(1) primary reactions, induced by reactor neutrons in elements other than the trace element to be assayed, or (2) second-order reactions, in which the neutrons induce reactions in the activation product and diminish its concentration in the sample.

This latter type of interference is not important in this program because the comparator samples correct for this effect.

Two types of primary interfering reactions are of importance to the determination of trace element concentrations in food ash. Several elements of interest in this program, such as barium and strontium, have activation products which are also formed as a result of the fission of  $U^{235}$ . The 54-day  $Sr^{89}$  and 85-min  $Ba^{139}$  isotopes exemplify this phenomenon. For these elements, however, other activation products, which do not result from the fission of uranium, are available for use. Therefore, the alternative isotopes, 65-day  $Sr^{85}$  and 11.6-day  $Ba^{131}$ , were selected. For some elements, discussed in a later section, this alternative selection is not possible. Therefore, appropriate measures are required to correct for any interference in such analyses due to fission reactions.

The second type of primary interference involves reactions of fast reactor neutrons with constituents of the matrix which result in production of charged particles. For example, if the trace element having atomic number  $Z$  is to be assayed, interference may result from an  $(n, p)$  reaction with element  $Z+1$  or from an  $(n, \alpha)$  reaction with element  $Z+2$ . The extent of such interference is dependent primarily on the relative concentrations of element  $Z$  and of the interfering elements. Since the effective cross-sections for the  $(n, p)$  and  $(n, \alpha)$  reactions are generally several orders of magnitude less than those for  $(n, \gamma)$  reactions, the interference is usually small.

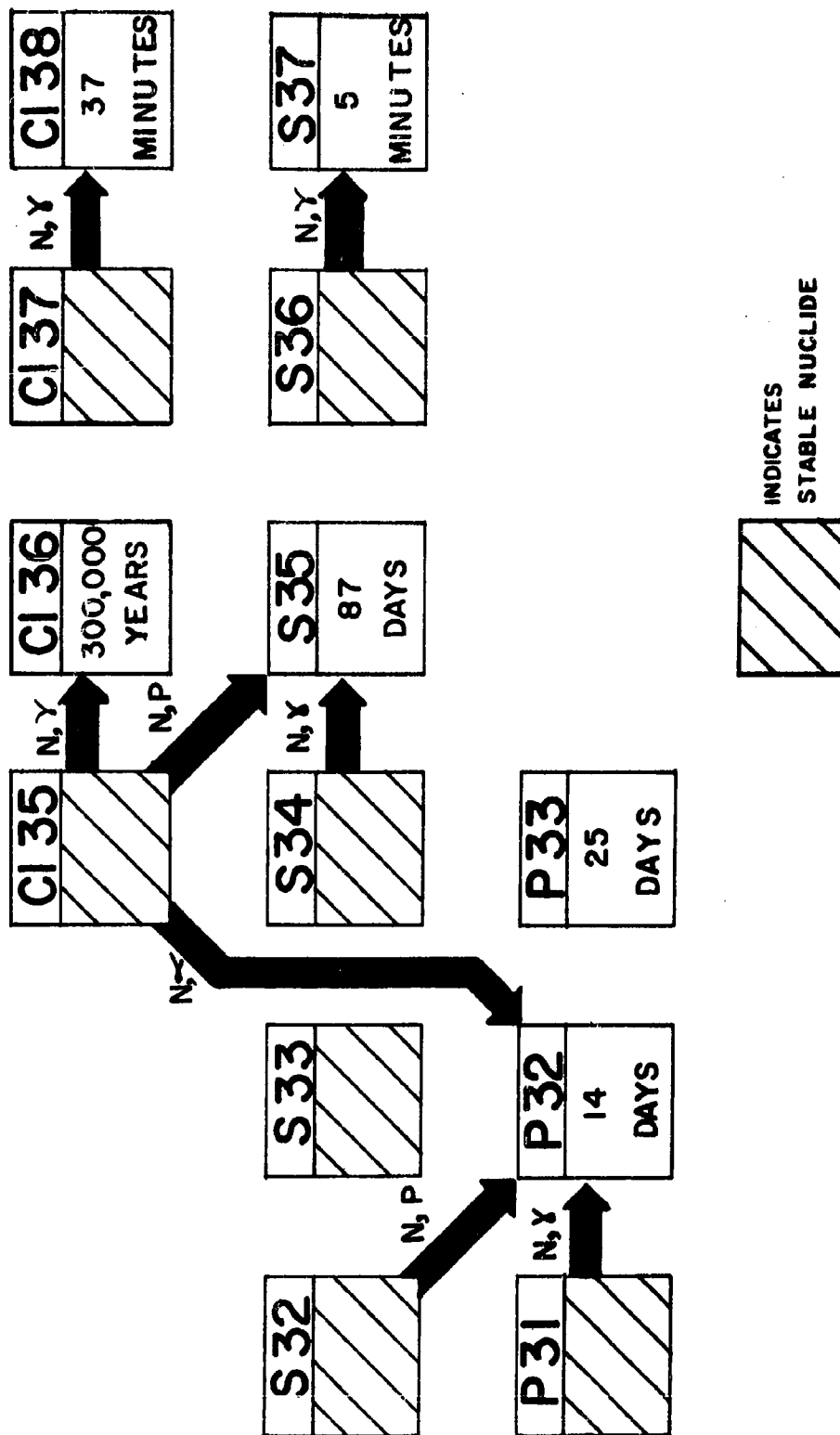
The correction which may be required can normally be determined experimentally by irradiation and analysis for the sought activation product in a standard comparator sample of the interfering element. Analysis is also required to determine the concentration of the interfering element in the matrix. From the known concentrations of the interfering element in the matrix and in the comparator, and from the measured quantity of the activation product in the comparator, a correction factor can be determined and applied.

The elements for which this correction may be required in this program are discussed in a later section. However, the analysis of three elements, sulfur, phosphorus and chlorine, for which the interference is very important, is described here as an example.

The pertinent section of the Chart of the Nuclides<sup>(5)</sup>, presented in Figure 1, shows the several possible neutron-induced reactions in these elements and the modes of interference with sulfur and phosphorus analyses. From Figure 1, it is seen that (n,  $\gamma$ ) reactions in chlorine yield the  $3 \times 10^5$ -year  $\text{Cl}^{36}$  and the 37-min  $\text{Cl}^{38}$ , while the (n, p) reaction in  $\text{Cl}^{35}$  yields 87-day  $\text{S}^{35}$ . The latter nuclide is also formed by the (n,  $\gamma$ ) reaction in  $\text{S}^{34}$ . Since the only other (n,  $\gamma$ ) activation reaction in sulfur yields the very short-lived  $\text{S}^{37}$ , measurement of  $\text{S}^{35}$  is required for neutron activation analysis for sulfur in food ash. Therefore, a correction for the potential interference from chlorine must be made.

Similarly, the only (n,  $\gamma$ ) activation product in phosphorus is 14.2-day  $\text{P}^{32}$  which is also produced by the  $\text{S}^{32}$ (n, p) reaction. Therefore, the mutual interference of these elements is unavoidable in this program, and a systematic experimental study to determine the extent of the interference was required. The detailed discussion of this problem is presented in Appendix I.

FIGURE 1 -- CHLORINE, SULFUR, AND PHOSPHORUS  
ACTIVATION



### Activation reactions

After evaluation of the above factors, neutron activation reactions were specified for the respective trace element analyses. Only  $(n, \gamma)$  reactions were selected for these elements, except for the determination of  $U^{235}$ . The resulting activation products for those elements for which analyses have been completed are shown in Table I along with data for possible interfering reactions. It can be noted, from column four of the table, that some interference may occur from  $(n, p)$  or  $(n, \alpha)$  reactions for most of the elements. However, with the exception of two or three elements, corrections for these interferences were expected to be minimal.

### Selection of Comparators

In this program, the concentrations of trace elements were measured using the comparator method. This method requires that primary comparators, for each trace element to be determined, be irradiated concurrently in the same position as the matrix samples. If interferences due to fission of  $U^{235}$  or to  $(n, p)$  or  $(n, \alpha)$  reactions on adjacent elements may occur, secondary comparators, containing the interfering element, are also required.

The comparators are prepared from known amounts of the respective elements or of their compounds. If a compound is used, it must have a definite stoichiometry and be stable under irradiation. In addition, care must be taken to avoid local flux disturbances by comparators for elements having large cross-sections for neutron activation.

The comparator materials selected are shown in Table II. The table summarizes the chemical form and typical weights of comparator samples which have been used in this program. The weights were chosen such that the amount of

TABLE I  
DATA FOR ACTIVATION PRODUCTS AND INTERFERING REACTIONS

Element	Activation Product	Radiation Measured	Interfering Reaction
Phosphorus	14.2-d $P^{32}$	1.707 Mev $\beta^-$	$S^{32}(n, p), Cl^{35}(n, \alpha)$
Sulfur	87-d $S^{35}$	0.1617 Mev $\beta^-$	$Cl^{35}(n, p)$
Chlorine	$3.0 \times 10^5$ -y $Cl^{36}$	0.714 Mev $\beta^-$	None
Scandium	83.9-d $Sc^{46}$	0.885 Mev $\gamma$	$Ti^{46}(n, p)$
Iron	45.1-d $Fe^{59}$	1.098 Mev $\gamma$	$Co^{58}(n, p)$
Cobalt	5.24-y $Co^{60}$	1.1728 Mev $\gamma$	$Ni^{60}(n, p)$
Zinc	245-d $Zn^{65}$	1.119 Mev $\gamma$	None
Selenium	127-d $Se^{75}$	0.402 Mev $\gamma$	None
Rubidium	18.66-d $Rb^{86}$	1.079 Mev $\gamma$	$Sr^{86}(n, p)$
Strontium	64-d $Sr^{85}$	0.513 Mev $\gamma$	None
Zirconium	65-d $Zr^{95}$	0.723, 0.756 Mev $\gamma$	U, Th fission
Ruthenium	39.8-d $Ru^{103}$	Mixed $\beta^-$	U, Th fission
Palladium	17-d $Pd^{103}$	Mixed $\gamma$	$Cd^{106}(n, \alpha)$
Indium	49-d $In^{114m}$	0.190 Mev $\gamma$	None
Tin	119-d $Sn^{113}$	0.393 Mev $\gamma$	$Sb^{123}(n, p)$
Tellurium	104-d $Te^{123m}$	0.158 Mev $\gamma$	None
Cesium	2.07-y $Cs^{134}$	0.796 Mev $\gamma$	$Ba^{134}(n, p)$
Barium	11.5-d $Ba^{131}$	0.214 Mev $\gamma$	None
Cerium	32.5-d $Ce^{141}$	Mixed $\gamma$	$Pr^{141}(n, p)$ U, Th fission
Hafnium	70-d $Hf^{175}$	0.089 Mev $\gamma$	None
Iridium	74.4-d $Ir^{192}$	Mixed $\beta^-$	$Pt^{192}(n, p)$
Platinum	4.3-d $Pt^{193m}$	Mixed $\beta^-$	None
Uranium-238	2.346-d $Np^{239}$	Mixed $\beta^-$	None
Uranium-235	12.8-d $Ba^{140}$	Mixed $\beta^-$ ( $La^{140}$ )	None

TABLE II  
DATA FOR COMPARATOR SAMPLES

Trace Element	Primary Comparator	Secondary Comparator	Typical Wt. of Element in Prim. Comp., mg
Phosphorus	$\text{Mg}_2\text{P}_2\text{O}_7$	S, NaCl	2.8
Sulfur	S	NaCl	23
Chlorine	NaCl	-	10.4
Scandium	$\text{Sc}(\text{NO}_3)_3$	Ti	0.001
Iron	Fe	Al-0.1% Co	9.8
Cobalt	Al-0.1% Co alloy	Ni	0.01
Zinc	Zn	-	11
Selenium	Se	-	1.0
Rubidium	RbCl	$\text{Sr}(\text{NO}_3)_2$	1.0
Strontium	$\text{Sr}(\text{NO}_3)_2$	-	20
Zirconium	$\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	-	10.3
Indium	In	Sn	0.12
Tin	Sn	Sb	22
Tellurium	Te	-	10
Cesium	$\text{CsNO}_3$	$\text{Ba}(\text{NO}_3)_2$	0.08
Barium	$\text{Ba}(\text{NO}_3)_2$	-	11
Hafnium	Hf	-	0.12
Uranium -235	Enriched U	-	0.01
Uranium -238	Natural $\text{U}_3\text{O}_8$	-	1.0

material used per sample would give much less than a one per cent attenuation of either the thermal or epithermal neutron flux.

### Irradiation Facility

The neutron irradiations for this program are being performed at the Brookhaven National Laboratory Research Reactor. An important factor in the choice of this reactor was the rather small value of the ratio of the fast to thermal neutron fluxes. A small ratio assists in minimizing the fast neutron induced (n, p) and (n,  $\alpha$ ) interfering reactions. The neutron fluxes, ranging up to  $\sim 2 \times 10^{13}$  n/cm<sup>2</sup>-sec, the two-week operating cycle, and the moderate cost for service irradiations and transportation of radioactive materials from BNL to the NSEC laboratories were also factors in the selection of this facility.

### EXPERIMENTAL PROGRAM

The objective of this experimental program is the neutron activation analysis of four foods, beef, pork, ham, and chicken, to determine trace element concentrations, and the determination of the radioactivity balances for both beta and gamma radiations to assist in characterization of the total neutron-induced radioactivity which may be produced during irradiation sterilization of these foods.

The experimental method involves sampling of the foods, preparation of the food and comparator samples for irradiation, irradiation of the samples, post-irradiation analyses, and evaluation and interpretation of the experimental data.

The basis for the selection of elements for study in this program has been discussed previously<sup>(1)</sup>. Due to the lack of definitive analytical data for concentrations of many elements in foods, the importance of certain groups of elements for this program and the technical and economic feasibility of their quantitative analysis by neutron activation techniques was in question. Two typical groups of such elements are the rare earths and the platinum metals. It was deemed desirable to perform qualitative activation analyses for these two groups to estimate their significance. Other elements, selected for study, are being determined quantitatively.

#### Sampling and Sample Preparation

Fifty pounds each of beef, pork, ham, and chicken were prepared by the QMFCI for this program. After removal of bones, cartilage, glands, and other matter normally considered inedible, each food was ground first through a 1/2" - 1.0" plate, followed by a second grinding through a 1/8" - 1/4" plate. The meat was then mixed by machine into a homogeneous mass, packaged, frozen, and shipped to the NSEC laboratories. It is being kept frozen until needed in the program.

Portions of each of the four homogenized foods were ashed to concentrate the inorganic constituents into samples suitable for analytical purposes. The foods were first partially ashed by slow combustion in large stainless steel vessels to remove volatile and liquid matter. This step was followed by ignition in large porcelain crucibles at 800°C. Care was taken in removing the partially ashed residue from the steel combustion vessels to avoid introduction of metal particles into the ash. The ratio of ash weight to bulk weight for each food was determined. The values, which varied from approximately 0.5 per cent to 2 per cent, are shown in Table III.



TABLE III  
WEIGHTS OF BULK AND ASHED FOODS

Food	Bulk Wt. (kg)	Ashed Wt. (gr)	Percent Ash
Chicken	11.55	71.2	0.62
Beef	11.47	69.9	0.70
Pork	11.41	52.0	0.46
Ham	11.10	220.6	2.0

Samples of the ashed foods and of the comparators for the respective trace elements were prepared and packaged for irradiation. Two-gram aliquots of the ash were packed tightly in cylinders of aluminum foil. These cylinders were tightly crimped and then sealed in quartz ampoules. Three samples of each food ash have been prepared for each irradiation.

Three primary comparator samples were prepared for each trace element to be assayed, along with secondary comparators for interfering elements. Only those chemical forms of the elements which have known stoichiometry and are stable with respect to thermal or radiolytic decomposition were considered for this application. The comparators were doubly-contained in aluminum foil and sealed quartz ampoules for irradiation. The data for the comparator samples are shown in Table II. The encapsulated ash and comparator samples were inserted in standard BNL aluminum irradiation cans prior to insertion in the reactor.

#### Irradiations

Several irradiations are required to carry out the analyses planned for this program. Elements which yield long-lived activation products are analyzed in samples subjected to relatively long irradiations. Those with shorter half-lives are best analyzed in samples subjected to less extensive irradiation. Each irradiation is conducted

for a specific period of time and at a neutron flux selected to optimize the production of the activation products in a particular range of half-life values.

Two irradiations have been performed prior to this report. Irradiation No. 1 was performed primarily to obtain (1) qualitative analysis data for the rare earths and the platinum metals, and (2) quantitative analysis data for uranium in each food. It was deemed desirable to obtain the qualitative analysis data at an early stage of the program to permit incorporation of quantitative analyses which might be indicated for these elements. The uranium data were also desired as early as possible to determine the extent to which the presence of fission products might interfere with the analyses of other trace elements in the ash samples. It was also convenient to determine cerium quantitatively in this irradiation concurrently with the other rare earths. In this irradiation, the samples were subjected to a neutron flux of  $8 \times 10^{12}$  n/cm<sup>2</sup>-sec for 2.9 days, or for an integrated neutron flux of  $1.9 \times 10^{18}$  n/cm<sup>2</sup>. Irradiation No. 2 was performed to obtain quantitative analysis data for selected trace elements whose activation products have half-lives greater than 10 days. The elements shown in Table II, with the exception of uranium, were analyzed in the samples from this irradiation. This irradiation was conducted for 21 days in a flux of  $\sim 7 \times 10^{12}$  n/cm<sup>2</sup>-sec for an equivalent integrated flux of  $1.3 \times 10^{19}$  n/cm<sup>2</sup>.

#### Post-Irradiation Analyses

After irradiation, the ash and comparator samples were returned to the NSEC laboratories for radiometric analysis of the selected neutron activation products. These analyses consisted of the dissolution of the ash and comparator samples, the specific radiochemical separation and purification of the respective activation products, and the measurement of their radiations. Special analyses are also being performed to derive the radioactivity balance data needed for complete characterization of the total radioactivity content of the ash samples.

### Dissolution methods

Two samples of each food ash from each irradiation were boiled with aqua regia for several hours to effect dissolution. In each case, an insoluble residue, presumably  $\text{SiO}_2$ , remained. The insolubles were filtered and weighed. The percentage of insolubles for the various ashes is shown in Table IV.

TABLE IV  
ASH RESIDUES AFTER AQUA REGIA TREATMENT

Food Ash	Chicken	Beef	Pork	Ham
Percent Insolubles	6.5	3.9	3.9	0.2

The residues were treated with a mixture of equal volumes of aqua regia and concentrated hydrofluoric acid (HF) until complete solution was obtained. Excess HF was removed by fuming the solution several times with 12 N HCl. The aqua regia leach and the solution of the insolubles were combined and made up to a known volume with 12 N HCl. The ash solutions were stored in polyethylene bottles.

A third sample of each ash from the second irradiation was treated in a special manner to permit chlorine determinations. These samples were dissolved in warm 4 N  $\text{HNO}_3$  in a closed system. The closed system consisted of an Erlenmeyer flask, fitted with a delivery tube which dipped into a 1 M NaOH solution. Any chlorine volatilized during the dissolution was retained in the NaOH. After dissolution, the two solutions were combined, made up to a known volume with 2 N  $\text{HNO}_3$ , and stored in a polyethylene bottle.

The metallic comparators, cobalt, nickel, titanium, tin, iron, and zinc, were dissolved in warm 6 N HCl and made up to a known volume with 3 N HCl. The tellurium comparator was dissolved in boiling aqua regia.

The sulfur comparator was dissolved in a mixture of fuming  $\text{HNO}_3$  and concentrated  $\text{HClO}_4$  in a closed system. Pot and the  $\text{NaOH}$  trap solutions were combined and boiled for several minutes with aqua regia again in a closed system. These precautions were necessary to avoid volatilization losses of sulfur (as  $\text{SO}_2$ ) and to oxidize all of the sulfur to sulfate ion.

The chlorine comparator was dissolved in water. However, for the determination of  $\text{S}^{35}$  in the chlorine comparator, an aliquot was boiled with aqua regia in a closed system after addition of a known amount of  $\text{H}_2\text{SO}_4$  as carrier. Again, pot and trap solutions were combined before dilution to a known volume.

All other comparators were dissolved in 6 N  $\text{HNO}_3$  and made up to volume with 3 N  $\text{HNO}_3$ . All comparator solutions were stored in polyethylene bottles.

#### Qualitative analyses

Qualitative analyses were performed for representative elements of the rare earths and the platinum metals in the samples from the first irradiation. Detailed analytical procedures are presented in Appendix II.

In summary, the rare earths were separated from the food ash solution by precipitation of the mixed fluorides. Subsequently, they were separated into the lanthanum and yttrium groups by extraction of the yttrium group with tributyl phosphate (TBP). The lanthanum group consists of those elements having atomic numbers from 57 through 63, exclusive of cerium, while the elements with atomic numbers from 64 through 71, along with yttrium and scandium, comprise the yttrium group. Gamma spectra of the separated fractions were obtained with a 256-channel pulse height analyzer at time intervals of several weeks. The occurrence of photopeaks in these spectra due to photons of specific energies and the change in the photopeak intensity with time provided a means of identification of certain nuclides in the samples. Therefore, estimates of the concentrations of some of these elements were possible.

The separations of the platinum metals were based on the scheme of analysis described by Noyes and Bray<sup>(6)</sup>. Analyses were performed for four elements, ruthenium, palladium, iridium, and platinum. Rhodium was not sought because it has no suitable activation product. No analyses were performed for osmium, because of its possible volatilization during the ashing process.

The ruthenium and iridium fractions were assayed by measurement of their beta radiations using an end-window, methane-flow proportional counter. The palladium and platinum fractions were assayed by measuring their gamma radiations on a single-channel pulse height analyzer biased to detect all photons in excess of 60 Kev. Purity of these fractions was ascertained by half-life measurements and by observation of their gamma radiations with a 256-channel pulse height analyzer.

For qualitative analyses, no comparator samples were used. Therefore, the estimates of the concentrations of the elements detected were calculated, using equation (2), from the known reactor irradiation conditions and the estimated counting efficiencies for the respective activation products.

#### Quantitative analyses

For quantitative analysis, for each trace element, three aliquots were taken from the solutions of the replicate irradiated ashes, and, after addition of predetermined quantities of the element as a carrier, specific radiochemical separation and purification procedures for the respective radionuclides were performed. In several instances, groups of similar elements were separated together prior to their final purification. In the case of zirconium and hafnium, which have nearly identical chemical properties, no attempt was made to separate them from each other. Their analysis in a mixture by gamma spectrometry has been described<sup>(7, 8)</sup>.

The replicate comparator samples were assayed for these elements by the same procedures used for the ash samples, except that, in some cases, simplification was possible. For those trace elements for which interfering activation reactions were anticipated, analyses for the activation product were also performed in comparator samples of the interfering element.

Radiometric measurements for the specific activation products were made in both the ash and comparator samples. The activation products utilized are shown in Table I. For each activation product, identical measurement methods were made in both types of samples. For most of the activation products, measurements of photopeaks due to specific photons were made by pulse height analysis techniques using either a single-channel or 256-channel pulse height analyzer. In the determination of phosphorus, sulfur, chlorine, and uranium ( $\text{Ba}^{140}$  and  $\text{Np}^{239}$ ), measurements of the beta radiations of the respective activation products were made using end-window, methane-flow proportional counters.

The detailed quantitative analytical procedures are presented in Appendix II. Some of these procedures were based on widely-used methods<sup>(9, 10, 11)</sup> with appropriate modifications for the needs of this program. In other cases, the analytical requirements necessitated more extensive purification operations, which were developed during the course of the work.

Radioactivity balance studies are being carried out to characterize in detail the total radioactivity content of the irradiated food ash as a function of decay time after irradiation. The total beta activity in each ash sample from Irradiation No. 2 is being determined by beta assay of aliquots of the unprocessed solution. The total gross gamma activity of these samples is determined by measurement of the total gamma activity due to photons having energies in excess of 60 Kev in a similar aliquot.

To characterize the total activities, a counting sample of each element assayed in the ash samples from this irradiation is being assayed periodically for beta and gamma activities under the same conditions as the aliquots of the original solutions.

Data obtained for the individual counting samples for beta radioactivity balances are converted to beta disintegrations per minute per gram of ash. The sum of the disintegration rates for the elements is then compared to the measured value of the total beta disintegration rate per gram of ash. The data for the gamma radioactivity balances are treated in an analogous manner.

## EXPERIMENTAL RESULTS

### Qualitative Analyses

The presence of several platinum metals and of several rare earths in meat ash has been established by qualitative neutron activation analysis.

103 192 193m  
were identified by the energies of their beta or gamma radiations and their half-lives. Estimates were made of the order of magnitude of the concentrations of these elements in the four foods. The values, which range from  $\sim 10^{-4}$  ppm to  $10^{-6}$  ppm in the bulk foods, are shown in Table V.

Identification of certain rare earth elements was made from gamma spectral analyses of the yttrium and lanthanum groups. Gamma spectra of the yttrium fraction from the beef ash sample are presented in Figure 2. Spectrum A was taken approximately two months after the irradiation, and spectrum B was taken after an additional two month decay. Spectra for the yttrium fractions from the other meat ash samples

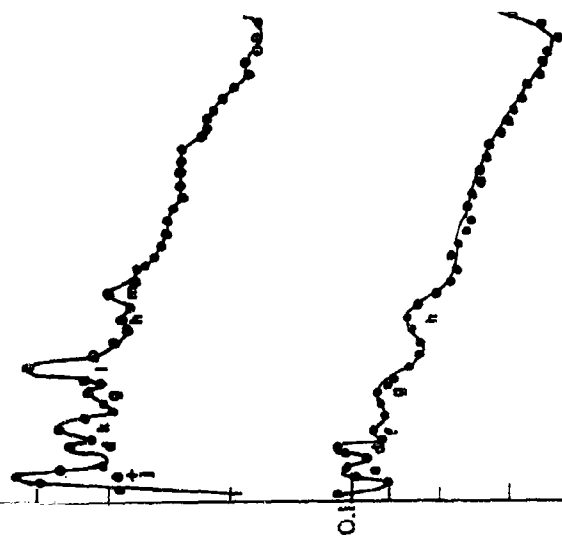
TABLE V  
CONCENTRATIONS OF TRACE ELEMENTS IN FOOD  
(Qualitative Analyses)

Chemical Group	Trace Element	CONCENTRATIONS (ppm)							
		Chicken		Beef		Pork		Ham	
		Bulk	Ash	Bulk	Ash	Bulk	Ash	Bulk	Ash
Platinum Metals	Ru	$6 \times 10^{-4}$	0.1	$7 \times 10^{-4}$	$10^{-2}$	$5 \times 10^{-4}$	0.1	$2 \times 10^{-3}$	$10^{-3}$
	Pd	$6 \times 10^{-4}$	0.1	$7 \times 10^{-4}$	$10^{-3}$	$5 \times 10^{-4}$	0.1	$2 \times 10^{-3}$	$10^{-3}$
	Ir	$6 \times 10^{-6}$	$10^{-3}$	$7 \times 10^{-6}$	$10^{-3}$	$5 \times 10^{-6}$	$10^{-3}$	$2 \times 10^{-5}$	$10^{-3}$
	Pt	$6 \times 10^{-4}$	0.1	$4 \times 10^{-4}$	$10^{-3}$	$5 \times 10^{-4}$	0.1	$2 \times 10^{-3}$	$10^{-3}$
Rare Earths Yttrium Group	Yb	$6 \times 10^{-5}$	$10^{-2}$	$7 \times 10^{-5}$	$10^{-3}$	$5 \times 10^{-6}$	$10^{-3}$	$2 \times 10^{-5}$	$10^{-3}$
	Tm	$6 \times 10^{-6}$	$10^{-3}$	$7 \times 10^{-6}$	$10^{-3}$	$5 \times 10^{-6}$	$10^{-3}$	$2 \times 10^{-5}$	$10^{-3}$
	Lu	$6 \times 10^{-5}$	$10^{-2}$	$7 \times 10^{-5}$	$10^{-2}$	$5 \times 10^{-6}$	$10^{-3}$	$2 \times 10^{-5}$	$10^{-3}$
	Eu	$6 \times 10^{-5}$	$10^{-2}$	$7 \times 10^{-5}$	$10^{-3}$	$5 \times 10^{-6}$	$10^{-3}$	$2 \times 10^{-5}$	$10^{-3}$
Lanthanum Group									



**FIGURE 2**  
GAMMA SPECTRA FOR YTTRIUM  
GROUP IN IRRADIATED BEEF ASH

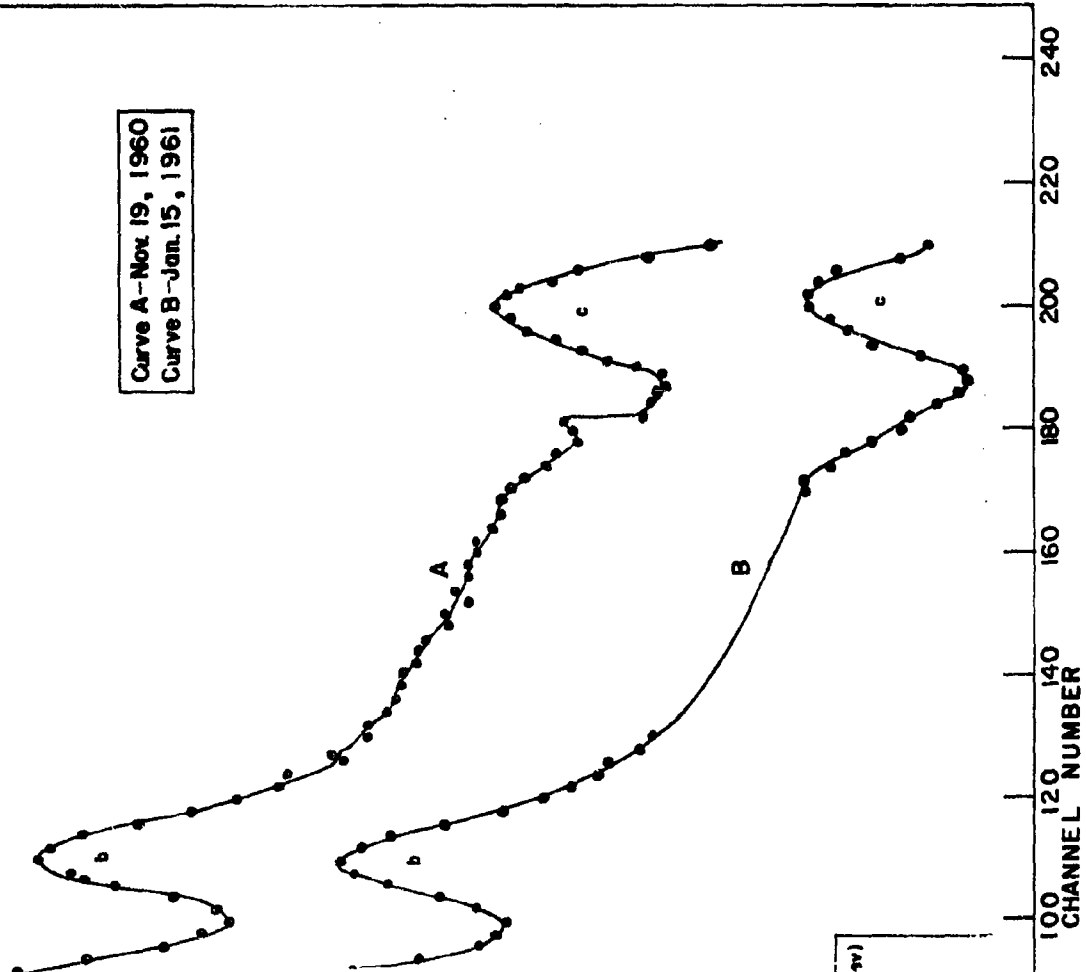
Curve A - Nov. 19, 1960  
Curve B - Jan. 15, 1961



RELATIVE COUNT RATE

-22-

a - Sc <sup>46</sup> (0.89 Mev)	g - Yb <sup>169</sup> (0.178 Mev)
b - Sc <sup>46</sup> (1.12 Mev)	h - Yb <sup>169</sup> (0.30 Mev)
c - Sc <sup>46</sup> (2.01 Mev)	j - Lu <sup>177</sup> (0.07 Mev)
d - Tm <sup>120</sup> (0.084 Mev)	k - Lu <sup>177</sup> (0.113 Mev)
e - Yb <sup>169</sup> (0.064 Mev)	l - Lu <sup>177</sup> (0.208 Mev)
f - Yb <sup>169</sup> (0.133 Mev)	m - Lu <sup>177</sup> (0.32 Mev)



are essentially the same. The most prominent photopeaks appear in channels 89, 110, and 200. These peaks correspond to gamma energies of 0.88 Mev, 1.12 Mev, and 2.0 Mev and are due to 85-day  $\text{Sc}^{46}$ . Although scandium follows yttrium group chemistry, its rather high concentration in these samples was unexpected. Therefore, a quantitative analysis for scandium was performed.

Because of the comparatively large amount of scandium activity in these spectra, the sensitivity for the detection of other components was decreased substantially. However, it was possible to identify photopeaks due the 84-Kev photon of 129-day  $\text{Tm}^{170}$ , and to several photons of 32-day  $\text{Yb}^{169}$  and 6.8-day  $\text{Lu}^{177}$ . Estimates were made of the order of magnitude of their concentrations in the four meats.

Gamma spectra for the lanthanum fraction from the beef ash sample are presented in Figure 3. These spectra were taken at the same time as those for the yttrium fraction. Again, spectra for the other ash samples were nearly identical. The most prominent photopeaks, corresponding to photon energies of 0.120 Mev, 0.34 Mev, 0.86 Mev, and 1.09 Mev, indicate the presence of 13-year  $\text{Eu}^{152}$  and 16-year  $\text{Eu}^{154}$ . There is also some evidence for a 20-Kev photon, which may indicate the presence of 80-year  $\text{Sm}^{151}$ .

Estimates were made of the concentrations of these rare earth elements in the four foods. The estimated values are of the order of  $10^{-6}$  to  $10^{-5}$  ppm in the bulk foods. The data are shown in Table V.

### Quantitative Analyses

The concentrations of twenty elements in each food ash have been determined in this phase of the program. The analytical data are shown in Table VI, along with the concentrations in the bulk foods which were calculated from the ratios of ash to bulk weight given in Table III. Definitive values have been obtained for all elements except sulfur and zirconium. The very large upper limits for the concentrations of

FIGURE 3  
GAMMA SPECTRA FOR LANTHANUM  
GROUP IN IRRADIATED BEEF ASH

Curve A Nov. 19, 1960  
Curve B Jan. 5, 1961

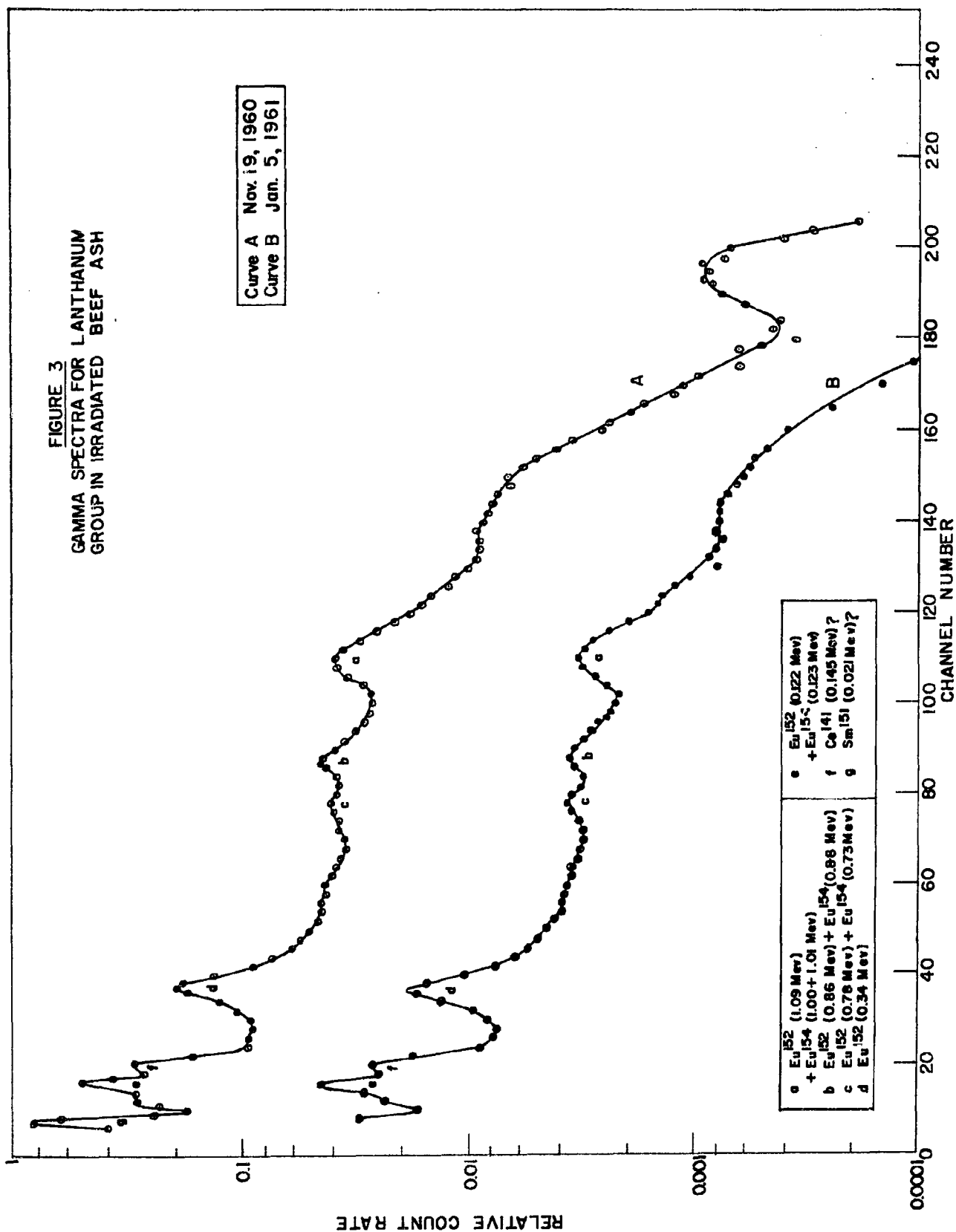


TABLE VI  
CONCENTRATIONS OF TRACE ELEMENTS IN FOOD  
(Quantitative Analyses)

Element	CONCENTRATIONS (ppm)							
	Chicken		Beef		Pork		Ham	
	Ash	Bulk	Ash	Bulk	Ash	Bulk	Ash	Bulk
Phosphorus	$2.0 \times 10^5$	$1.2 \times 10^5$	$1.9 \times 10^5$	$1.3 \times 10^3$	$2.0 \times 10^5$	$9.2 \times 10^2$	$5.2 \times 10^4$	$1.0 \times 10^3$
Sulfur	$< 2 \times 10^4$	$< 1 \times 10^2$	$< 8 \times 10^4$	$< 6 \times 10^2$	$< 4 \times 10^4$	$< 2 \times 10^2$	$< 5 \times 10^5$	$< 1 \times 10^{-4}$
Chlorine	$3.2 \times 10^3$	20	$1.8 \times 10^4$	$1.3 \times 10^2$	$9.2 \times 10^3$	42	$9.9 \times 10^4$	$2.0 \times 10^2$
Scandium	1.2	$7.4 \times 10^{-3}$	0.79	$5.5 \times 10^{-3}$	0.57	$2.6 \times 10^{-3}$	0.12	$2.4 \times 10^{-3}$
Iron	$2.1 \times 10^4$	$1.3 \times 10^2$	$5.8 \times 10^3$	41	$4.2 \times 10^3$	19	$3.9 \times 10^3$	78
Cobalt	17	0.11	4.5	$3.2 \times 10^{-2}$	4.0	$1.8 \times 10^{-2}$	3.0	$5.9 \times 10^{-2}$
Zinc	$1.7 \times 10^3$	11	$2.9 \times 10^3$	20	$3.0 \times 10^3$	14	$4.8 \times 10^2$	9.5
Selenium	$6.6 \times 10^{-2}$	$4.1 \times 10^{-4}$	$3.9 \times 10^{-2}$	$2.7 \times 10^{-4}$	$1.7 \times 10^{-2}$	$7.8 \times 10^{-5}$	$1.3 \times 10^{-2}$	$2.6 \times 10^{-4}$
Rubidium	$3.9 \times 10^3$	24	$1.8 \times 10^2$	1.3	$2.8 \times 10^2$	1.3	$7.5 \times 10^2$	15
Strontium	35	0.22	25	0.18	20	$9.2 \times 10^{-2}$	19	0.38
Zirconium	$< 16$	$< 0.10$	$< 24$	$< 0.2$	$< 30$	$< 0.1$	$< 5$	$< 0.1$
Indium	0.75	$4.7 \times 10^{-3}$	1.3	$9.2 \times 10^{-3}$	0.47	$2.2 \times 10^{-3}$	0.55	$1.1 \times 10^{-2}$
Tin (a)	17	0.11	77	0.54	14	$6.4 \times 10^{-2}$	3.2	$6.4 \times 10^{-2}$
Tellurium	$1.0 \pm 0.5$	$(6 \pm 3) \times 10^{-3}$	$0.7 \pm 0.14$	$(5 \pm 1) \times 10^{-3}$	$0.7 \pm 0.14$	$(3 \pm 0.6) \times 10^{-3}$	$1.0 \pm 0.2$	$(2.0 \pm 0.4) \times 10^{-2}$
Cesium	1.7	$1.1 \times 10^{-2}$	1.3	$9.2 \times 10^{-3}$	1.3	$6.0 \times 10^{-3}$	0.33	$6.6 \times 10^{-3}$
Barium	53	0.33	50	0.35	38	0.21	19	0.38
Cerium	$(1.7 \pm 0.4) \times 10^{-3}$	$(1.1 \pm 0.3) \times 10^{-5}$	$(5.4 \pm 1.4) \times 10^{-4}$	$(3.8 \pm 1.0) \times 10^{-6}$	$(3.9 \pm 1.0) \times 10^{-3}$	$(1.8 \pm 0.4) \times 10^{-5}$	$(7.5 \pm 1.9) \times 10^{-4}$	$(1.5 \pm 0.4) \times 10^{-5}$
Hafnium	3.1	$1.9 \times 10^{-2}$	3.9	$2.0 \times 10^{-2}$	4.2	$1.9 \times 10^{-2}$	0.60	$1.2 \times 10^{-2}$
Uranium (235)	$(6.0 \pm 0.9) \times 10^{-3}$	$(3.6 \pm 0.5) \times 10^{-5}$	$(3.8 \pm 0.6) \times 10^{-3}$	$(2.7 \pm 0.4) \times 10^{-5}$	$(3.3 \pm 0.5) \times 10^{-3}$	$(1.5 \pm 0.2) \times 10^{-5}$	$(1.5 \pm 0.2) \times 10^{-3}$	$(3.0 \pm 0.4) \times 10^{-5}$
Uranium (238)	$1.1 \pm 0.2$	$(6.8 \pm 1.0) \times 10^{-3}$	$0.50 \pm 0.07$	$(3.5 \pm 0.5) \times 10^{-3}$	$0.48 \pm 0.07$	$(3.4 \pm 0.5) \times 10^{-3}$	$0.19 \pm 0.03$	$(3.8 \pm 0.6) \times 10^{-3}$

sulfur are indicative of the extreme interference of the  $\text{Cl}^{35}(\text{n}, \text{p})\text{S}^{35}$  reaction.

The reported value of the upper limit is the sulfur concentration which corresponds to the minimum quantity of sulfur-produced  $\text{S}^{35}$  that is detectable in the presence of the chlorine-produced  $\text{S}^{35}$  in each sample. For the three foods, chicken, pork, and beef, the total  $\text{S}^{35}$  found was identical, within experimental error, to the chlorine-produced  $\text{S}^{35}$ . In the case of ham ash, the minimum detectable quantity of sulfur is unrealistically high. Therefore, in each case, it is concluded that chlorine interference precludes determination of sulfur in the ash samples by neutron activation analysis.

Zirconium was determined in a purified mixture of zirconium and hafnium by gamma spectrometry techniques. The hafnium photopeaks in the spectrum were sufficiently predominant to mask the  $\text{Zr}^{95}$  photopeaks. The values of the upper limits for zirconium concentrations were calculated from estimates of the minimum quantity of  $\text{Zr}^{95}$  that could be detected in the presence of the hafnium activity in each sample. The limiting values for zirconium concentrations are high relative to the observed hafnium concentrations because the zirconium cross-section is much smaller than that of hafnium.

With reference to Table I, it is seen that ten elements for which analytical results are reported in Table VI are free from interfering reactions. Corrections for interfering reactions have been incorporated, where required, in the results for all of the other elements with the exception of scandium, tin, and cobalt. Correction factors for these latter elements are not yet available because the concentrations of the respective interfering elements, titanium, antimony, and nickel, have not yet been determined. Therefore, the results reported for these three elements are subject to revision. However, results for the other seventeen elements are considered final.

It is of interest to compare the ratios of  $\text{U}^{235}$  and  $\text{U}^{238}$  concentrations in the ash samples. These ratios are shown in Table VII. The ratios agree, within experimental error, with the value for naturally-occurring uranium isotopes.<sup>(5)</sup>

TABLE VII  
ISOTOPIC RATIOS OF URANIUM IN FOOD ASH

Ashed Food	$\frac{U^{235}}{U^{238}}$
Chicken	$(5.7 \pm 1.4) \times 10^{-3}$
Beef	$(7.6 \pm 1.4) \times 10^{-3}$
Pork	$(6.8 \pm 1.5) \times 10^{-3}$
Ham	$(7.9 \pm 1.6) \times 10^{-3}$
Natural	
Abundance	$7.1 \times 10^{-3}$

In general, precisions of replicate analyses were maintained to better than  $\pm 5$  per cent. On the basis of these precisions and of the evaluation of possible consistent errors in sample preparation and analysis, it is estimated that the concentrations of most of the trace elements have been determined with an accuracy of  $\pm 10$  per cent. All results shown in Table VI are judged to have this accuracy except where larger errors are given.

#### Radioactivity Balance Studies

Radioactivity balance data have been obtained for the four ash samples from Irradiation No. 2 in a continuing program, commencing on October 20, 1960. This date represents a decay time of 13 days after irradiation. The decay of the aliquots of the unprocessed ash solutions has been observed since that date to determine the characteristics of the total gross beta and gross gamma radioactivities induced in the ashes during the irradiation. The individual decay of the beta and gamma

radioactivity in counting samples of each of the seventeen elements analyzed has also been observed. These decay curves have been extrapolated to the initial assay date of the total radioactivity samples.

The summation of the beta decay curves for the individual elements, in terms of beta disintegration per minute per gram of ash, as a function of decay time yields a gross beta decay curve for the activation products of the elements whose concentrations have been determined. Similarly, summation of the gamma radioactivity decay curve yields the gross gamma decay curve for the same activation products.

Two activation products, 14.2-day  $P^{32}$  and 87-day  $S^{35}$ , constitute a large fraction of the beta radioactivity in the irradiated ashes. The sum of these two radioactivities contributes in excess of 95 per cent of the sum of the beta radioactivities of the known activation products in each sample throughout this decay period.

The principal component of the total gamma radioactivity during the first two months of the decay period is the bremsstrahlung from the beta radiations of  $P^{32}$ . During the latter portion of the period, the gamma radiations of 245-day  $Zn^{65}$ , 45-day  $Fe^{59}$ , and/or 5.2-year  $Co^{60}$  become equally important.

Comparison of the gross decay curves of the identified neutron activation products with the respective decay curves of the total radioactivity in the ash is still in progress. It is deemed important to continue these observations throughout the contract period to gain additional information on the contributions of the longer-lived components which will have increasing relative significance with increasing decay time. Detailed data for the radioactivity balances will be presented at the conclusion of the study.

## DISCUSSION AND RECOMMENDATIONS

Quantitative neutron activation analyses have been carried out for twenty elements in samples of ashed chicken, beef, pork, and ham. These analyses have yielded definitive values for the concentrations of fifteen of the elements. The concentrations in bulk foods have ranged from values of  $\sim 1,000$  ppm for phosphorus to  $\sim 10^{-6}$  ppm for cerium. Sensitivity limitations precluded the determination of the concentrations of two elements, sulfur and zirconium. Therefore, maximum values for their concentrations, based on the limit of sensitivity of the methods employed, are reported.

Values reported for scandium, cobalt, and tin are presently subject to corrections for interfering reactions from titanium, nickel, and antimony, respectively, when the concentrations of these latter elements in the ash samples are determined. Analyses for these three elements is, therefore, deemed desirable in future irradiations.

Qualitative neutron activation analyses have resulted in detection of several noble metal and rare earth elements. Estimated values for the concentrations of some of these elements range from  $10^{-3}$  ppm to  $10^{-6}$  ppm in the bulk foods.

The reported values for chlorine in the ash samples are considered accurate to  $\pm 10$  per cent. However, the apparent concentrations of chlorine in the bulk foods may be in error due to the possible volatilization of chlorine during the ashing operation. Analysis of the bulk food for chlorine would be required to determine its fractional loss, if any, during ashing.

The special problems associated with the determination of phosphorus and sulfur are discussed in detail in Appendix I. The chlorine concentrations in these samples precluded determination of sulfur concentrations. In general, the values of the sulfur concentrations are a prerequisite to determination of phosphorus. However, on the basis of the observed phosphorus concentrations and of the analyses for  $P^{32}$  in the sulfur comparators, an estimate was made of the sulfur concentration



required in each ash sample to introduce a 10 per cent error in the phosphorus analysis. The estimated sulfur concentrations were 63 per cent in ham ash and were in excess of 100 per cent for the other ashes. Since these concentrations are not possible, it can be stated that no significant error was introduced in the phosphorus analyses by neglecting the effects of sulfur interference. Therefore, the analytical data for phosphorus in these samples appear valid.

Phosphorus concentrations in the beef, pork, and chicken ashes were determined to be  $\sim 20$  per cent. This concentration implies that the ash is essentially 100 per cent  $\text{Ca}_3(\text{PO}_4)_2$ , if it is assumed that all of the phosphorus is present in this chemical form. This concentration is equivalent to a calcium concentration of approximately 52 per cent. The typical concentration range for calcium in ashed food and vegetation is from 2 to 25 per cent<sup>(14)</sup>, which corresponds to phosphorus concentrations of  $\sim 1$  to 12 per cent, if the elements are present as  $\text{Ca}_3(\text{PO}_4)_2$ . The value for the phosphorus concentration in ham ash is consistent with this range of values. The higher phosphorus concentrations in the other three ashes may indicate either (1) that the composition of these ashes is essentially  $\text{Ca}_3(\text{PO}_4)_2$ , or (2) that the phosphate present in the ash is chemically combined with two or more cationic elements. The determination of the concentrations of calcium and other abundant cations, such as sodium and potassium, in these samples may clarify this question. These analyses are recommended as a portion of a complete analysis of the important constituents in these four foods.

In summary, it is recommended that a group of ten additional elements be analyzed by neutron activation methods to provide a set of analytical data for the potentially important constituents of these four homogenized foods. These elements are calcium, sodium, potassium, manganese, titanium, nickel, copper, arsenic, antimony, and cadmium. Data for sodium, potassium, and calcium are required because they are known to be important constituents in foods and, therefore, contribute significantly to the total neutron induced radioactivity<sup>(2)</sup>. Titanium, nickel, and antimony are required to confirm tentative data already obtained for scandium,

cobalt, and tin, respectively, as well as for their individual concentrations. Analysis for cadmium is recommended because it is activated not only by neutrons but also by the  $(\gamma, \gamma')$  reaction with  $\text{Co}^{60}$  photons. The remaining three elements may have significant concentrations which would yield large quantities of shorter-lived activation products.

Since the results of this program constitute a unique body of data for elemental compositions of foods, a more complete analytical program is also recommended. Such a program should include analyses for chromium, gallium, and germanium, to provide complete data for the medium weight elements, and also for approximately seven heavy elements, such as silver, tantalum, tungsten, gold, thallium, lead and bismuth. These heavy elements are important because (1) they have large neutron activation cross-sections or (2) they have relatively large probabilities for activation by gamma rays of moderate energies. Thus, they are potentially important sources of radioactivity in irradiated foods.

Radioactivity balance data should also be obtained in future irradiations for complete characterization of these foods. In addition, it is recommended that the radioactivity balance data for Irradiation No. 2 be extended for a period of from 12 to 18 months decay time.

The four foods under investigation are being characterized carefully both with respect to trace element concentrations and neutron-induced radioactivity content. It has been recommended previously<sup>(1)</sup> that this characterization study be extended to several elements having natural radioactivity (e.g.,  $\text{Po}^{210}$ ,  $\text{Ra}^{226, 228}$ ,  $\text{Ac}^{227}$ ,  $\text{K}^{40}$ ,  $\text{Pb}^{210}$ ) and to nuclides which are present in fallout of radioactive debris from the atmosphere (e.g.,  $\text{Sr}^{90}$ ,  $\text{Cs}^{137}$ ,  $\text{Pu}^{239}$ ). Such analyses would, of course, be performed on portions of the unirradiated ash.

Since samples of these foods are being employed for related programs of interest to the Quartermaster Food and Container Institute, it is recommended that the QMFCI consider the complete characterization of these four foods with respect to their trace element concentrations and their natural and irradiation-induced radioactivities.

## CONTRACT STATUS

It is estimated that approximately 70 per cent of the Scope of Work of this contract had been completed at the end of this report period. It is further estimated that, effective that date, 94 per cent of the funds had been expended. It is anticipated that essentially 100 percent of the funds will have been expended with the completion of this report. Experimental work has been interrupted pending clarification of the exact amount of unexpended funds.

The expenditure of labor and funds in excess of that anticipated to complete the Scope of Work to date was due, in part, to unforeseen technical difficulties. Detailed information has already been transmitted to the QMFCI in a separate document.

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## APPENDIX I

### ACTIVATION ANALYSIS FOR PHOSPHORUS AND SULFUR

Neutron activation analysis for phosphorus, using the activation reaction  $P^{31}(n, \gamma)P^{32}$ , is complicated by the possible interference of sulfur and/or chlorine in the matrix sample from the fast neutron reactions  $S^{32}(n, p)P^{32}$  and  $Cl^{35}(n, \alpha)P^{32}$ , as indicated in Figure 1. Similarly, activation analysis for sulfur, using the reaction  $S^{34}(n, \gamma)S^{35}$ , is subject to interference from the reaction  $Cl^{35}(n, p)S^{35}$ . Since 14.2-day  $P^{32}$  is the only neutron activation product available for phosphorus, and 87-day  $S^{35}$  is the only sulfur activation product with a half-life of useful magnitude for many applications, neutron activation analysis techniques for these two elements must take into account the need for corrections in the analytical data for the effects of the interfering elements.

Since the total quantity of  $S^{35}$  produced during the irradiation of the matrix is the sum of the contributions from the  $S^{34}(n, \gamma)S^{35}$  and  $Cl^{35}(n, p)S^{35}$  reactions, it is necessary to differentiate between the  $S^{35}$  produced by these two reactions. This can be accomplished by measuring the total  $S^{35}$  content of the matrix and the  $S^{35}$  produced from the chlorine in the matrix. The  $S^{35}$  produced from the sulfur in the matrix is the difference between these two quantities.

To make these measurements, the concentration of chlorine in the matrix must be determined by some method. Activation analysis, using the reaction  $Cl^{35}(n, \gamma)Cl^{36}$ , was the method chosen for this program.

In a similar manner, in analysis for phosphorus, the total quantity of  $P^{32}$  must be determined along with the quantities produced by the  $S^{32}(n, p)P^{32}$  and the  $Cl^{35}(n, \alpha)P^{32}$  reactions, respectively. The amount of  $P^{32}$  due to activation of phosphorus is the balance remaining after subtraction of the contributions of the two interfering reactions from the total  $P^{32}$  found. Therefore, the concentrations of both sulfur and chlorine must be known in order to compute the concentration of phosphorus. The methods used for these determinations are detailed below.

## SULFUR ANALYSES

Sulfur analyses require the irradiation of comparator samples for both sulfur and chlorine along with the ash samples. The data required and the method of obtaining them are shown in Table VIII.

If the ratio of the concentration of chlorine to sulfur in the ash is relatively large, the calculation performed in Operation No. 5a in Table VIII may result in a small difference term of two large numbers. The smallest statistically-significant value of this difference represents the minimum quantity of sulfur-produced  $S^{35}$ /gram ash that is detectable in the sample. If this value is used in the calculation in Operation No. 7a in the table, a value for the upper limit of the sulfur concentration in the ash is obtained.

## PHOSPHORUS ANALYSES

In general, neutron activation analyses for phosphorus require data for the concentrations of sulfur and chlorine in the matrix sample and for the production of  $P^{32}$  from chlorine and sulfur comparators. Therefore, these comparators must be irradiated along with the matrix and the phosphorus comparators. The data required and the corresponding experimental operations are shown in Table IX.

TABLE VIII  
METHOD OF ANALYSIS FOR SULFUR

Data Required	Experimental Operation
1. Cl concentration in ash ( $\mu\text{g Cl/gr ash}$ )	1a Determine $\text{Cl}^{36}$ in ash (dpm $\text{Cl}^{36}/\text{gr ash}$ ) 1b Determine $\text{Cl}^{36}$ in Cl comparator (dpm $\text{Cl}^{36}/\mu\text{g Cl}$ ) 1c Calculate Cl concentration, using equation (1)
2. $\text{S}^{35}$ production from Cl (dpm $\text{S}^{35}/\mu\text{g Cl}$ )	2a Determine $\text{S}^{35}$ in Cl comparator (dpm $\text{S}^{35}/\mu\text{g Cl}$ )
3. $\text{S}^{35}$ production from Cl in ash (dpm $\text{S}^{35}(\text{Cl})/\text{gr ash}$ )	3a Calculate: item (2) x item (1)
4. Total $\text{S}^{35}$ production in ash (dpm $\text{S}^{35}/\text{gr ash}$ )	4a Determine $\text{S}^{35}$ in ash (dpm $\text{S}^{35}/\text{gr ash}$ )
5. $\text{S}^{35}$ production from S in ash (dpm $\text{S}^{35}(\text{S})/\text{gr ash}$ )	5a Calculate: item (4) - item (3)
6. $\text{S}^{35}$ production from S (dpm $\text{S}^{35}/\mu\text{g S}$ )	6a Determine $\text{S}^{35}$ in sulfur comparator (dpm $\text{S}^{35}/\mu\text{g S}$ )
7. S concentration in ash ( $\mu\text{g S/gr ash}$ )	7a Calculate: item (5) $\div$ item (6)

TABLE IX  
METHOD OF ANALYSIS FOR PHOSPHORUS

Date Required	Experimental Operations
1. Cl concentration in ash ( $\mu\text{g Cl/gr ash}$ )	1a See Operation No. 1c, Table VIII
2. S concentration in ash ( $\mu\text{g S/gr ash}$ )	2a See Operation No. 7a, Table VIII
3. $\text{P}^{32}$ production from Cl ( $\text{dpm P}^{32}/\mu\text{g Cl}$ )	3a Determine $\text{P}^{32}$ in Cl comparator ( $\text{dpm P}^{32}/\mu\text{g Cl}$ )
4. $\text{P}^{32}$ production from Cl in ash ( $\text{dpm P}^{32}(\text{Cl})/\text{gr ash}$ )	4a Calculate: item (3) x item (1)
5. $\text{P}^{32}$ production from S ( $\text{dpm P}^{32}/\mu\text{g S}$ )	5a Determine $\text{P}^{32}$ in S comparator ( $\text{dpm P}^{32}/\mu\text{g S}$ )
6. $\text{P}^{32}$ production from S in ash ( $\text{dpm P}^{32}(\text{S})/\text{gr ash}$ )	6a Calculate: item (5) x item (2)
7. Total $\text{P}^{32}$ production in ash ( $\text{dpm P}^{32}/\text{gr ash}$ )	7a Determine $\text{P}^{32}$ in ash ( $\text{dpm P}^{32}/\text{gr ash}$ )
8. $\text{P}^{32}$ production from P in ash ( $\text{dpm P}^{32}(\text{P})/\text{gr ash}$ )	8a Calculate: item (7) - $\frac{1}{2}$ item (6) + item (4)
9. $\text{P}^{32}$ production from P ( $\text{dpm P}^{32}/\mu\text{g P}$ )	9a Determine $\text{P}^{32}$ in P comparator ( $\text{dpm P}^{32}/\mu\text{g P}$ )
10. P concentration in ash ( $\mu\text{g P/gr ash}$ )	10a Calculate: item (8) $\div$ item (9)



The extent to which sulfur or chlorine may interfere in the phosphorus analysis is a function of the relative concentrations of the three elements. If the concentration of either sulfur or chlorine is much higher than that of phosphorus, the difference term in Operation No. 8a may be less than the statistical error of the other terms. In this case, analysis for phosphorus would be precluded. The limit of sensitivity for a given sample would then be determined in a manner analogous to that described for sulfur.

A special type of interference due to a second-order neutron reaction may also interfere in analyses for phosphorus. If large quantities of silicon are present, the reaction<sup>(12)</sup>,  $\text{Si}^{30}(n, \gamma)\text{Si}^{31} \xrightarrow{\beta^-} \text{P}^{31}(n, \gamma)\text{P}^{32}$ , may enhance the production of  $\text{P}^{32}$  and yield apparent phosphorus concentrations which are too large. However, it has been shown<sup>(13)</sup> that this reaction is not important in samples containing very high silicon concentrations which were irradiated under similar conditions at the Brookhaven National Laboratory reactor. Therefore, it is estimated that this effect was important in these samples.

## APPENDIX II

### ANALYTICAL PROCEDURES

#### THE PLATINUM METALS

##### Preliminary Separations

To an aliquot of the sample solution, the following carriers are added:  $\text{Ru}^{+3}$  (as  $\text{RuCl}_3$ ),  $\text{Ir}^{+3}$  (as  $\text{IrCl}_3$ ),  $\text{Pt}^{+4}$  (as  $\text{H}_2\text{PtCl}_6$ ), and  $\text{Pd}^{+2}$  (as  $\text{Pd}(\text{NO}_3)_2$ ). An equal volume of 3 N HCl is added to the solution, and  $\text{SO}_2$  is bubbled through it for about 5 minutes. The solution is boiled while about 5 ml of a 3 per cent solution of  $\text{H}_2\text{O}_2$  is added dropwise. The boiling is continued for 3 more minutes. The hot solution is saturated with  $\text{H}_2\text{S}$  until it has cooled to room temperature to precipitate the mixed sulfides. The sulfides are dissolved in aqua regia and 15 ml concentrated  $\text{HClO}_4$  and 5 ml  $\text{HNO}_3$  are added, and  $\text{RuO}_4$  is distilled into a trap containing 6 N NaOH and ethyl alcohol.

The distillation residue is evaporated to dryness and taken up in 12 N HCl. After saturating the solution with HCl gas,  $(\text{NH}_4)_2\text{PtCl}_6$  and  $\text{NH}_4\text{IrCl}_6$  are precipitated by addition of a saturated  $\text{NH}_4\text{Cl}$  solution. The supernate is saturated with chlorine gas to precipitate  $(\text{NH}_4)_2\text{PdCl}_6$ .

The mixed platinum and iridium salts are dissolved in aqua regia, the solution is boiled to dryness and taken up in a minimum amount of water, 6 N  $\text{Na}_2\text{CO}_3$ , and bromine. Hydrated  $\text{IrO}_2$  is precipitated.  $(\text{NH}_4)_2\text{PtCl}_6$  is then precipitated from the supernate with 12 N HCl and a saturated solution of  $\text{NH}_4\text{Cl}$ .

### Ruthenium

The mixed ruthenium oxides which are formed by reduction of  $\text{RuO}_4$  by the ethanol in the alkaline trap solution are dissolved in 12 N  $\text{HCl}$ . After addition of holdback carriers for iridium, platinum, and palladium, and of solid  $\text{NaBiO}_3$ ,  $\text{RuO}_4$  is again distilled. The resulting precipitate is dissolved in 12 N  $\text{HCl}$ , and metallic ruthenium is precipitated from 3 N  $\text{HCl}$  by reduction with zinc. The precipitate is washed with water, ethyl alcohol, and ether, and weighed as the metal. The  $\text{Ru}^{103, 106}$  mixture is determined by beta counting.

### Iridium

The hydrated  $\text{IrO}_2$  from the separation procedure is dissolved in aqua regia. The solution is boiled nearly to dryness and taken up in 12 N  $\text{HCl}$ . Holdback carriers for ruthenium, palladium, and platinum are added, and  $(\text{NH}_4)_2\text{PtCl}_6$  and  $(\text{NH}_4)_2\text{IrCl}_6$  are precipitated. The precipitate is dissolved in aqua regia; the solution is boiled almost to dryness and taken up in water. After adding 6 M  $\text{Na}_2\text{CO}_3$ , two  $\text{Fe}(\text{OH})_3$  scavenging precipitations are performed, after which the solution is heated and bromine water is added to precipitate hydrated  $\text{IrO}_2$ . The  $\text{IrO}_2$  is dissolved in aqua regia, the solution is brought to almost dryness and the residue is taken up in 12 N  $\text{HCl}$ . After addition of a small quantity of platinum carrier, the Ir-Pt separation is repeated. Finally  $\text{IrO}_2$  is dissolved in 5 ml aqua regia, made  $\sim 4$  N in  $\text{HCl}$ , heated, and saturated with  $\text{H}_2\text{S}$  to precipitate  $\text{IrS}_2$ . Iridium is weighed as the sulfide, 74-day  $\text{Ir}^{192}$  is assayed by beta counting.

### Platinum

The  $(\text{NH}_4)_2\text{PtCl}_6$  precipitate from the initial separation procedure is dissolved in aqua regia, and holdback carriers for iridium, ruthenium, and palladium are added. Then the solution is boiled almost to dryness, and  $(\text{NH}_4)_2\text{PtCl}_6$  and  $(\text{NH}_4)_2\text{IrCl}_6$  are precipitated. After an  $\text{IrO}_2$  scavenging precipitation, the platinum-iridium-palladium separation cycle is repeated. The final  $(\text{NH}_4)_2\text{PtCl}_6$  precipitate is again dissolved in aqua regia, evaporated to dryness, and taken up in 12 N HCl. The  $\text{Pt}^{+4}$  is reduced to  $\text{Pt}^{+2}$  with  $\text{SnCl}_2$  (Note 1), and extracted into amyl acetate. The organic layer is washed three times with an equal volume 9 N HCl and platinum is back-extracted into water. The aqueous solution is adjusted to 2 N in HCl, tin holdback carrier and oxalic acid are added, and PtS is precipitated with  $\text{H}_2\text{S}$ . The PtS precipitate is washed with water, alcohol, and ether prior to weighing. The mixed platinum radioactivities are assayed by pulse height analysis.

### Palladium

The  $(\text{NH}_4)_2\text{PdCl}_6$  precipitate from the initial separation procedures is dissolved in aqua regia. After addition of holdback carriers for ruthenium, palladium, and iridium, the solution is evaporated almost to dryness and is taken up in 0.4 N HCl. Palladium is precipitated with dimethylglyoxime. The precipitate is washed thoroughly with warm 0.5 N HCl and is then dissolved in aqua regia. After a second dimethylglyoxime precipitation in the presence of ruthenium, platinum, and iridium holdback carriers, the aqua regia solution is boiled to destroy glyoxal. The solution is then adjusted to about 2 N in HCl, and from the hot solution PdS is precipitated with  $\text{H}_2\text{S}$ . The precipitate is washed with water, alcohol and ether prior to weighing as PdS. The mixed palladium activities are assayed by pulse height analysis.

## THE RARE EARTHS

### Group Separations

Cerium, as ceric ion, yttrium, and lanthanum carriers are added to an aliquot of the sample along with holdback carrier for zirconium.  $\text{H}_2\text{O}_2$  was added to reduce the  $\text{Ce}^{+4}$  to  $\text{Ce}^{+3}$ . The solution is adjusted to about 4 N in  $\text{HCl}$  and 1 N in  $\text{HF}$ . The resulting precipitate of rare earth is washed several times with a mixture of 4 N  $\text{HCl}$  and 1 N  $\text{HF}$ . The fluorides are dissolved in 16 N  $\text{HNO}_3$  containing  $\text{H}_3\text{BO}_3$ . After addition of zirconium holdback carrier, the rare earth fluorides are reprecipitated and dissolved. The mixed hydroxides are precipitated with ammonia and after several washes with 1 N  $\text{NH}_4\text{OH}$ , the precipitate is dissolved in 16 N  $\text{HNO}_3$ . The yttrium sub-group (Note 2) is extracted into a 60 per cent tributylphosphate (TBP) solution in benzene. The lanthanum sub-group (and cerium) remain in the aqueous phase.

### The Yttrium Sub-group

The TBP extract is washed several times with an equal volume of 16 N  $\text{HNO}_3$ , and the yttrium sub-group is then back-extracted into water. The solution is neutralized against methyl red with concentrated  $\text{NH}_4\text{OH}$ , buffered with ammonium acetate and the oxalates are precipitated with  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ . The precipitate is washed with water, ethyl alcohol, and ether, dried in a vacuum, and weighed as  $\text{Y}_2(\text{C}_2\text{O}_4)_3 \cdot 10 \text{H}_2\text{O}$ . The mixed gamma radiations are assayed by pulse height analysis.

### Cerium

The aqueous phase from the TBP extraction is washed once with an equal amount of diethylether to remove any suspended TBP. The aqueous phase is evaporated almost to dryness and taken up in 6 N  $\text{HNO}_3$ . Cerium is oxidized to the ceric state by adding about 250 mg solid  $\text{KBrO}_3$ .  $\text{Ce}(\text{IO}_3)_4$  is precipitated with 0.3 M  $\text{HIO}_3$ . The rest of the lanthanum sub-group elements remain in the supernate. The  $\text{Ce}(\text{IO}_3)_4$  is dissolved in 12 N  $\text{HCl}$  containing  $\text{H}_2\text{O}_2$ . The solution is evaporated almost to dryness, 6 N  $\text{HNO}_3$  and lanthanum holdback carrier are added, and  $\text{Ce}(\text{IO}_3)_4$  is again precipitated. The solution is neutralized against methyl red with  $\text{NH}_4\text{OH}$ , buffered with ammonium acetate and acetic acid, and cerium is precipitated by addition of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ . The precipitate is washed with water, alcohol, and ether, dried in a vacuum and weighed as  $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10 \text{H}_2\text{O}$ . The 32-day  $\text{Ce}^{141}$  is assayed by counting of its 0.142 Mev gamma radiation.

### The Lanthanum Sub-group

Cerium carrier is added to the supernate from the above  $\text{Ce}(\text{IO}_3)_4$  precipitation and a  $\text{Ce}(\text{IO}_3)_4$  scavenging precipitation is carried out by addition of  $\text{KBrO}_3$ . The greater part of the iodate in the supernate is reduced to iodide with  $\text{SO}_2$ . Iodide and iodate react to give iodine which is boiled out. After precipitation of the lanthanum group hydroxides with  $\text{NH}_3$ , the precipitate is dissolved in  $\text{HCl}$ , buffered with ammonium acetate and acetic acid, and the lanthanum sub-group is precipitated with  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ . The precipitate is washed with water, alcohol, and ether, dried in a vacuum, and weighed as  $\text{La}_2(\text{C}_2\text{O}_4)_3 \cdot 10 \text{H}_2\text{O}$ . The mixed gamma radiations are assayed by pulse height analysis.

## PHOSPHORUS

Phosphorus carrier as  $\text{H}_3\text{PO}_4$  (Note 3) is added to an aliquot of the dissolved ash, and the acidity is adjusted to about 1 N in  $\text{HNO}_3$ . The solution is heated to boiling, and ammonium phosphomolybdate is precipitated. After washing with 1 N  $\text{HNO}_3$ , the precipitate is dissolved in 6 N  $\text{NH}_4\text{OH}$  and made acidic to phenolphthalein. Addition of magnesia mixture (Note 4) precipitates  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ . The precipitate is digested in an ice bath for about 20 minutes, washed with cold 1 N  $\text{NH}_4\text{OH}$ , dissolved in 6 N  $\text{HCl}$ , diluted to about 15 ml and reprecipitated by addition of magnesia mixture and  $\text{NH}_4\text{OH}$ . The precipitate is again digested in an ice bath for at least 20 minutes, transferred to a weighed filter paper with cold 1 N  $\text{NH}_4\text{OH}$  and washed repeatedly with ethyl alcohol and ether. Air is sucked through the precipitate for  $5 \pm 0.5$  minutes, after which the precipitate is allowed to stand in air for 20 to 60 minutes before weighing as  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ . The 1.71-Mev beta radiation of  $\text{P}^{32}$  is counted through a 23 mg/cm<sup>2</sup> aluminum absorber to minimize interference from the 0.249-Mev beta radiations from any 25-day  $\text{P}^{33}$  which might be present.

Counting samples for  $\text{P}^{32}$  in phosphorus comparators are prepared by adding phosphorous carrier to aliquots of the phosphorus comparator solutions and precipitating  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ . Counting samples for  $\text{P}^{32}$  in sulfur and chlorine comparators are prepared by processing aliquots of the sulfur and chlorine comparators like ash samples.

## Sulfur

Sulfur carrier, as  $\text{H}_2\text{SO}_4$ , is added to an aliquot of the dissolved ash, and  $\text{BaSO}_4$  is precipitated. The precipitate is transferred to a porcelain crucible with a minimum amount of water and mixed with two to five grams of zinc dust. The slurry is dried and then heated to a dull red color for  $5 \pm 1$  minutes. After cooling, the mixture is transferred to a small distillation apparatus. About 25 ml of 4 M  $\text{HCl}$  are added to the flask and  $\text{H}_2\text{S}$  is distilled into a trap containing a 2 per cent  $\text{Cu}(\text{NO}_3)_2$  solution. The resulting  $\text{CuS}$  is filtered, washed with boiling water, ethyl alcohol, and ether, and weighed.  $\text{Sr}^{35}$  is assayed by counting its 0.167-Mev beta radiations. Correction is made for the variation of attenuation of the weak beta radiations with counting sample thickness by comparison to standard self-absorption curve. This curve was determined from a series of counting samples, having varying thicknesses and constant specific activity, and calibrated by a standardized  $\text{S}^{35}$  solution.

Counting samples for  $\text{S}^{35}$  in sulfur comparators are made by processing aliquots of the sulfur comparators like an ash sample. Counting samples for  $\text{S}^{35}$  in chlorine comparators are prepared by boiling aliquots of the chlorine comparators with aqua regia in the presence of sulfur carrier in a closed system and then carrying the combined pot and trap solutions through the sulfur procedure as described above.



## Chlorine

Chlorine carrier, as NaCl, is added to an aliquot of the solution which is then made approximately 6 N in  $\text{H}_2\text{SO}_4$ . After two  $\text{BaSO}_4$  scavenging steps, the solution is transferred to a distillation apparatus. Twenty milliliters of 36 N  $\text{H}_2\text{SO}_4$  are added, and HCl is distilled into a  $\text{AgNO}_3$  solution made slightly acidic with  $\text{HNO}_3$ . The resulting AgCl precipitate is dissolved in concentrated  $\text{NH}_4\text{OH}$ . After two  $\text{Fe}(\text{OH})_3$  scavenging precipitations, AgCl is reprecipitated with 6 M  $\text{HNO}_3$ . The last precipitation is performed in a large volume of solution at room temperature to obtain the finely divided precipitate desired for an optimum counting sample. The AgCl is washed with water, ethyl alcohol, and ether and weighed.  $\text{Cl}^{36}$  is assayed by measuring its 0.714-Mev beta radiations. Chlorine comparator samples are prepared by processing aliquots of the chlorine comparator solution like solutions of irradiated ash.

## Scandium

Scandium carrier, as  $\text{ScCl}_3$ , is added to an aliquot of the dissolved ash along with a few milligrams of zirconium holdback carrier.  $\text{Zr}(\text{IO}_3)_4$  is precipitated from 16 N  $\text{HNO}_3$  by addition of a saturated iodic acid solution. The supernate, containing the scandium, is evaporated to a volume of a few milliliters to expell excess nitric acid. After dilution to about 25 ml with water, the solution is saturated with  $\text{SO}_2$  to reduce part of the  $\text{HIO}_3$  to iodide, and the  $\text{I}_2$  is volatilized. A second  $\text{Zr}(\text{IO}_3)_4$  scavenging precipitation is performed. After removal of  $\text{I}_2$ ,  $\text{Sc}(\text{OH})_3$  is precipitated by saturating the solution with ammonia. The  $\text{Sc}(\text{OH})_3$  is dissolved in 6 N HCl, a few milligrams of iron carrier, as ferric ion, are added, and the iron is extracted into diethyl ether previously equilibrated with 6 N HCl. Subsequently,  $\text{Sc}(\text{OH})_3$  is precipitated from the aqueous layer and

dissolved in 12 N HCl. Scandium is then extracted into tributyl-phosphate (TBP). The organic layer is washed several times with 12 N HCl. Scandium is re-extracted into water, precipitated as  $\text{Sc}(\text{OH})_3$ , ignited and weighed as  $\text{Sc}_2\text{O}_3$ . The 85-day  $\text{Sc}^{46}$  is assayed by pulse height analysis of its 0.885-Mev and 1.119-Mev gamma radiations.

Aliquots of the scandium comparator solutions are used as scandium comparator samples. Counting samples for scandium in titanium comparators are obtained by applying the above procedure to aliquots of the titanium comparators, but omitting the initial  $\text{Zr}(\text{IO}_3)_4$  scavenging steps.

### Iron

Iron carrier, as  $\text{Fe}^{+3}$  ion, is added to an aliquot of the ash solution along with holdback carriers for cobalt and zinc. The solution is repeatedly evaporated almost to dryness with 12 N HCl, adjusted to 6 N in HCl, and adsorbed on a 100-200 mesh Dowex-1 anion exchange column (resin bed dimensions: 150 mm long, 12 mm diameter) which was previously equilibrated with 6 N HCl. After cobalt is eluted with 6 N HCl, iron is eluted with 0.5 N HCl. The fraction of the eluate containing the iron is evaporated almost to dryness, adjusted to 6 N in HCl, and extracted into an equal volume of ethyl ether, equilibrated with 6 N HCl. The ether layer is washed twice with ether-equilibrated 6 N HCl. The iron is back-extracted into water and precipitated as  $\text{Fe}(\text{OH})_3$ . The precipitate is digested in 2 ml of warm  $(\text{NH}_4)\text{H}_2\text{PO}_4$  reagent (Note 5) for a few minutes. Complete dissolution is effected by addition of 10 ml of  $(\text{NH}_4)_2\text{CO}_3$  reagent (Note 6). The warm solution is introduced into an electrolysis apparatus and iron is electroplated on a weighed platinum disk with a current of about 0.1 amps at  $\sim 3$ -6 volts. The plate is washed with water, ethyl alcohol, and ether and weighed. The 45-day  $\text{Fe}^{59}$

is assayed by pulse height analysis of its 1.10-Mev and 1.29-Mev gamma radiations.

Aliquots of the iron comparator solutions are used as iron comparator samples. Counting samples for iron in cobalt comparators are prepared by separating iron from cobalt by an anion exchange step as described above.

### Cobalt and Zinc

Both elements are separated from the same aliquot. Cobalt and zinc carriers, along with a few milligrams of iron holdback carrier, are added to an aliquot of the ash solution. Two  $\text{Fe}(\text{OH})_3$  scavenging precipitations are performed. The ammoniacal supernate is saturated with  $\text{H}_2\text{S}$  to precipitate  $\text{CoS}$  and  $\text{ZnS}$ . The precipitate is dissolved in a mixture of about 12  $\text{N}$   $\text{HCl}$  and a few drops of 3 per cent  $\text{H}_2\text{O}_2$ . The solution is concentrated and adsorbed on a Dowex-1 anion exchange column previously equilibrated with 6  $\text{N}$   $\text{HCl}$ . Cobalt is eluted with 6  $\text{N}$   $\text{HCl}$ , the column is then washed with two column volumes of water, and finally zinc is eluted with 2  $\text{N}$   $\text{NH}_4\text{OH}$ .

A few milligrams of zinc and iron holdback carriers are added to the cobalt fraction of the eluate. The elements are adsorbed on a Dowex-1 anion exchange column in the manner described previously. Cobalt is eluted from the column with 6  $\text{N}$   $\text{HCl}$ . Addition of 10  $\text{N}$   $\text{KOH}$  to the eluate precipitates  $\text{Co}(\text{OH})_2$  which, in turn, is dissolved in 6  $\text{N}$  acetic acid. The cobalt is then precipitated as  $\text{K}_3\text{Co}(\text{NO}_2)_6$  by addition of 3  $\text{N}$  acetic acid saturated with  $\text{KNO}_2$ . The precipitate is dissolved in a few milliliters of 12  $\text{N}$   $\text{HCl}$  and the solution is evaporated almost to dryness and fumed with 36  $\text{N}$   $\text{H}_2\text{SO}_4$ . The  $\text{CoSO}_4$  is dissolved in water and an electroplating solution is added (Note 7). The cobalt is

electroplated on a tared platinum disc at 0.1 amps and 3-5 volts, washed with water, ethyl alcohol, and ether, and weighed as the metal. The cobalt is assayed by pulse height analysis of its complex gamma radiations.

To prepare cobalt comparator samples, aliquots of the cobalt comparator solutions are plated on platinum discs after adding a few milligrams of cobalt carrier. Samples for cobalt in nickel comparators are prepared by separating cobalt from nickel by an anion exchange step.

The zinc fraction of the eluate is evaporated to dryness and taken up in 6 N HCl. Cobalt and iron holdback carriers are added, and the anion exchange separation is repeated. The eluate containing the zinc is again evaporated, made 1 N in HNO<sub>3</sub>, cooled in an ice bath, and ZnHg(SCN)<sub>4</sub> is precipitated by addition of 5 ml of K<sub>2</sub>Hg(SCN)<sub>4</sub> reagent (Note 8). The precipitate is washed with water, ethyl alcohol, and ether, and weighed. The 245-day Zn<sup>65</sup> is assayed by pulse height analysis of its 1.12-Mev gamma radiations.

Aliquots of the zinc comparator solution are used as zinc comparator samples.

#### Selenium

Selenium carrier (Note 9) is added to an aliquot of the ash solution adjusted to 3 N in HCl. The solution is saturated with SO<sub>2</sub> to precipitate elemental selenium. The precipitate is thoroughly washed with 0.5 N HCl, dissolved in a mixture of 12 N HCl and a few drops of bromine, and introduced into a ruthenium distillation apparatus. SeBr<sub>4</sub> is distilled from a hydrobromic acid medium containing 16 N HNO<sub>3</sub> and 36 N H<sub>2</sub>SO<sub>4</sub>. The SeBr<sub>4</sub> vapors are trapped in concentrated H<sub>2</sub>SO<sub>3</sub> in an ice-cooled water bath. The resulting selenium precipitate is washed with H<sub>2</sub>O, dissolved and reprecipitated. The final precipitate is washed with water, ethyl alcohol, and ether, dried and weighed as the metal. The 127-day Se<sup>75</sup> is

assayed by measurement of its complex mixture of gamma radiations.

Aliquots of the selenium comparator solutions are used as selenium comparator samples.

#### Rubidium (or Cesium)

Rubidium carrier, as  $\text{RbNO}_3$ , is added to an aliquot of the ash solution and is fumed with  $\text{HClO}_4$ . After the solution is allowed to cool,  $\text{RbClO}_4$  is precipitated by addition of ethyl alcohol. The precipitate is dissolved in water, a few milligrams of iron carrier are added, and a  $\text{Fe}(\text{OH})_3$  is precipitated with 6 N  $\text{NaOH}$ . After a second  $\text{Fe}(\text{OH})_3$  scavenging precipitation, the supernate is fumed with  $\text{HClO}_4$ .  $\text{RbClO}_4$  and some  $\text{NaClO}_4$  are again precipitated by addition of ethyl alcohol. The precipitate is washed thoroughly several times with warm ethyl alcohol to remove any coprecipitated  $\text{NaClO}_4$ . The final precipitate is washed with ether, dried, and weighed as  $\text{RbClO}_4$ . The 18.6-day  $\text{Rb}^{86}$  is assayed by pulse height analysis of its 1.08-Mev gamma radiations. The rubidium comparators were counted without any chemical treatment.

The cesium procedure used is identical to that for rubidium except cesium carrier is used. The 2.3-year  $\text{Cs}^{134}$  is assayed by pulse height analysis of its complex gamma radiations. Aliquots of the rubidium and cesium comparator solutions are used as rubidium and cesium comparators, respectively. Counting samples for rubidium in strontium and cesium in barium are prepared by separating the alkaline earths from the alkali metals by two carbonate precipitations.

### Strontium and Barium

Strontium and barium carriers, as the nitrates, are added to the same aliquots of the ash solution. The mixed nitrates are precipitated twice with ice-cold fuming nitric acid, and then are dissolved in water. A few milligrams of iron carrier are added, and  $\text{Fe}(\text{OH})_3$  is precipitated by saturating the solution with  $\text{NH}_3$ . After a second  $\text{Fe}(\text{OH})_3$  scavenging precipitation, the supernate is adjusted to pH 4, by making the solution acidic to methyl red indicator with 6 N  $\text{HNO}_3$  and adding 4 ml of 6 M ammonium acetate and 2 ml of 6 M acetic acid. The solution is heated nearly to boiling and  $\text{BaCrO}_4$  is precipitated with potassium dichromate. This precipitate is reserved for barium analysis.

Strontium is precipitated, as  $\text{SrCO}_3$ , from the supernate with  $\text{Na}_2\text{CO}_3$ . The precipitate is washed and dissolved in 6 N  $\text{HNO}_3$ . Approximately 10 milligrams of barium carrier are added, the solution again is adjusted to pH 4, and  $\text{BaCrO}_4$  is precipitated. After precipitation of  $\text{SrCO}_3$  from the supernate, the precipitate is washed with water, dried, and weighed. The 65-day  $\text{Sr}^{85}$  is assayed by pulse height analysis of its 0.513-Mev gamma radiation.

The initial  $\text{BaCrO}_4$  precipitate from the strontium procedure is washed with hot water and dissolved in 6 N  $\text{HNO}_3$ . After adding approximately 10 milligrams of strontium holdback carrier, the pH of the solution is adjusted to 4, and  $\text{BaCrO}_4$  is reprecipitated. The precipitate is washed with water, ethyl alcohol, and ether and weighed. The 11.6-day  $\text{Ba}^{131}$  is assayed by pulse height analysis of its complex gamma radiations.

Aliquots of the strontium and barium comparator solutions are used as strontium and barium comparator counting samples, respectively.

### Indium

Indium carrier, as  $\text{In}(\text{NO}_3)_3$ , is added to an aliquot of the ash solution along with holdback carriers for tin, antimony, bismuth, and tellurium. The solution is adjusted to  $\sim 2 \text{ N}$  in  $\text{HCl}$  and is saturated with  $\text{H}_2\text{S}$  to precipitate  $\text{Bi}_2\text{S}_3$ . After the  $\text{Bi}_2\text{S}_3$  scavenging precipitation is repeated, the supernate is saturated with  $\text{NH}_3$  to precipitate  $\text{In}_2\text{S}_3$ . After the  $\text{In}_2\text{S}_3$  is washed thoroughly with water, it is dissolved in  $6 \text{ N}$   $\text{HNO}_3$ , the solution is evaporated to dryness, taken up in 5 ml concentrated  $\text{HBr}$  and brought to dryness again. The residue is dissolved in  $4.5 \text{ N}$   $\text{HBr}$ , and indium is extracted into an equal volume of diethylether which is pre-equilibrated with  $4.5 \text{ N}$   $\text{HBr}$ . The organic phase is washed twice with  $4.5 \text{ N}$   $\text{HBr}$ . Indium is re-extracted into an equal volume of  $6 \text{ N}$   $\text{HCl}$ . The volume of the aqueous phase is reduced to about 0.5 ml, and water is added to adjust the solution to pH 1.  $\text{In}_2\text{S}_3$  is precipitated with  $\text{H}_2\text{S}$ . The  $\text{In}_2\text{S}_3$  is dissolved in  $6 \text{ N}$   $\text{HNO}_3$  and the extraction cycle is repeated. A final  $\text{In}_2\text{S}_3$  precipitate is washed with water, ether alcohol, and ether, dried, and weighed. The 49-day  $\text{In}^{114\text{m}}$  is assayed by pulse height analysis of its complex gamma radiations. Aliquots of the indium comparator solutions are used as indium comparator samples.

### Tin

Tin carrier, as  $\text{SnCl}_2$ , is added to an aliquot of the ash solution along with holdback carriers for antimony, zinc, cobalt, iron, and scandium. The solution is adjusted to  $1 \text{ N}$  in  $\text{HCl}$  and tin is precipitated as the sulfide with  $\text{H}_2\text{S}$  after addition of bromine. The precipitate is dissolved in  $12 \text{ N}$   $\text{HCl}$ , about 10 milligrams of antimony carrier is added, and the solution is adjusted to  $2.5 \text{ N}$  in  $\text{HCl}$ . After an antimony sulfide scavenging precipitation is performed from a boiling solution,

1 milliliter of concentrated  $\text{NH}_4\text{OH}$  is added to the supernate and  $\text{SnS}_2$  is precipitated with  $\text{H}_2\text{S}$ . The  $\text{SnS}_2$  is dissolved in a minimum volume of 12  $\text{N}$   $\text{HCl}$ . The solution is made basic with 6  $\text{N}$   $\text{NaOH}$ , and two  $\text{Fe}(\text{OH})_3$  scavenging precipitations are performed. Tin is then precipitated from the supernate with cupferron. The precipitate is washed, ignited, and weighed as  $\text{SnO}_2$ . The 112-day  $\text{Sn}^{113}$  is assayed by pulse height analysis of its 0.393-Mev gamma radiations.

Aliquots of the tin comparator solutions are used as tin comparator samples. Counting samples for tin in antimony are prepared as follows: To a suitable aliquot of the antimony comparator solution, antimony and tin carriers are added, then the solution is made 2  $\text{N}$  in  $\text{HCl}$ . Metallic antimony is precipitated upon addition of  $\sim 2$  grams finely divided iron powder. The supernate is concentrated, antimony carrier is added, and antimony metal is precipitated again by iron powder. This antimony scavenging step is repeated once more. Tin finally is precipitated as the cupferron chelate, ignited to  $\text{SnO}_2$ , mounted, and counted.

### Uranium

The uranium isotope of major abundance,  $\text{U}^{238}$ , was determined by measuring the amount of  $\text{Np}^{239}$  formed by the  $\text{U}^{238}(\text{n}, \gamma)\text{U}^{239}$  reaction.  $\text{U}^{235}$  was determined by measuring the amount of  $\text{Ba}^{140}$  produced by neutron-induced fission of  $\text{U}^{235}$ .

The procedure utilized to separate 12.8-day  $\text{Ba}^{140}$  from the ash solutions and from the  $\text{U}^{235}$  comparators is the same as described in the section "Strontium and Barium." The decay product of  $\text{Ba}^{140}$ , 40.8-hour  $\text{La}^{140}$ , is the nuclide on which the determination of  $\text{U}^{235}$  is based. The  $\text{La}^{140}$  is separated as  $\text{La}(\text{OH})_3$  approximately two weeks after preparation of the food and comparator barium samples. The  $\text{La}^{140}$  counting samples are  $\text{La}_2(\text{C}_2\text{O}_4)_3 \cdot 10 \text{H}_2\text{O}$ . The  $\text{La}^{140}$  is assayed by counting its complex beta radiations.



$\text{Np}^{237}$ , an alpha emitter with a half-life of  $2.2 \times 10^6$  years, is added, as a tracer, to an aliquot of the ash solution. Several drops of 30 per cent  $\text{H}_2\text{O}_2$  are added, and the solution is adjusted to  $\sim 6 \text{ N}$  in  $\text{HCl}$ . Two milliliters of concentrated formic acid and 2 ml 1  $\text{M}$   $\text{N}_2\text{H}_2 \cdot 2\text{HCl}$  solution are added, the solution is adjusted to 1.5  $\text{N}$  in  $\text{HCl}$ , and the mixture is boiled gently for about 10 minutes. Neptunium is extracted into a 0.4  $\text{M}$  solution of thenoyltrifluoroacetone (TTA) in benzene. The organic extract is washed with 2  $\text{N}$   $\text{HCl}$ . The neptunium is back-extracted into an aqueous phase by equilibrating the organic solution twice with 8  $\text{N}$   $\text{HCl}$ . The extraction cycle is repeated, and its combined extracts are fumed with  $\text{H}_2\text{SO}_4$ . After cooling, the solution is neutralized against methyl red with  $\text{NH}_4\text{OH}$ . The solution is made acidic with 2-3 milliliters 6  $\text{M}$   $\text{H}_2\text{SO}_4$  and about one gram of  $(\text{NH}_4)_2\text{SO}_4$  is added. Neptunium is electrodeposited on a platinum disc at 0.1 amp and 3 to 4 volts. To determine the chemical yield, the alpha particles of  $\text{Np}^{237}$  are counted on a 2- $\pi$  methane flow proportional counter. The beta radiations of 2.33-day  $\text{Np}^{239}$  are measured with an end-window, methane-flow proportional counter.

The comparators for  $\text{U}^{238}$  are processed exactly like the ash samples.

## NOTES

1.  $\text{SnCl}_2$  solution is prepared by dissolving  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in sufficient warm 12 N  $\text{HCl}$  to result in a 3 N  $\text{HCl}$  solution after dilution to volume.
2. The yttrium sub-group contains all rare earths with  $63 < Z < 71$ , i.e., Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y. The lanthanum sub-group (which correctly should be called Ce group) contains all rare earths with  $57 < Z < 63$  (i.e., La, Ce, Pr, Nd, Pm, and Sm). The reason for calling this the "lanthanum sub-group" is that cerium is separated prior to preparation of the actual counting sample.
3. Phosphorus carrier is prepared by dissolving the element in 16 N  $\text{HNO}_3$ .
4. Magnesia mixture is prepared by dissolving 50 grams of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and 100 grams of  $\text{NH}_4\text{Cl}$  in about 500 milliliters  $\text{H}_2\text{O}$ . The solution is made slightly basic with  $\text{NH}_4\text{OH}$  and allowed to stand overnight. After filtration, the solution is made slightly acidic with  $\text{HCl}$  and diluted to one liter.
5. The  $\text{NH}_4\text{H}_2\text{PO}_4$  reagent is prepared by dissolving 230 grams  $\text{NH}_4\text{H}_2\text{PO}_4$  in one liter of water.
6. The  $(\text{NH}_4)_2\text{CO}_3$  reagent is prepared by dissolving 393 grams of  $(\text{NH}_4)_2\text{CO}_3$  in 175 milliliters of 15 N  $\text{NH}_4\text{OH}$  and diluting to one liter.
7. The cobalt plating solution is prepared by mixing 5 milliliters of  $(\text{NH}_4)_2\text{SO}_4$  solution (50 mg/l) and 10 milliliters of 15 N  $\text{NH}_4\text{OH}$ .
8. The  $\text{K}_2\text{Hg}(\text{SCN})_4$  reagent is prepared by dissolving 39 grams  $\text{KSCN}$  in 200 milliliters of water. Into this solution 27 grams  $\text{HgCl}_2$  are stirred while diluting to one liter.
9. Selenium carrier solution is prepared by dissolving elemental selenium in 15 N nitric acid. Prolonged boiling is necessary to dissolve the selenium quantitatively. In this solution selenium presumably occurs in the tetra-valent state as  $\text{H}_2\text{SeO}_3$ .